Self-bonding characterization of non-wood lignocellulosic materials(Dissertation_全文)

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CHAPTER I

GENERAL INTRODUCTION

1.1 Development of binderless board

Adhesive has been accepted as the highest prices in the manufacturing of composites. The synthetic adhesives are derived from non-renewable petro source. Because of environmental concerns, the search of alternative adhesives has been widespread around the world.[1] Many researchers have tried to develop resin binder derived from renewable resources such as lignocellulosic materials (lignin, tannin, carbohydrates, etc). Even no-binder technology was explored since in the mid eighties.[2,3] It was suggested that binderless boards will become important products, especially in countries, which have no or limited wood resources and no adequate chemical industries but a surplus of agricultural residues.[4]

A number of studies have been published regarding the manufacture of binderless board, and they usually divided by three groups: the hot-pressing system, steam explosion process followed by hot pressing system, and steam-injection pressing. Wet-process hardboard is a kind of binderless board. An adhesive of less than 2% of dry board weight is usually added during the production.[5] During the mid-1980s, Shen[2] developed and patented a steam–explosion process of lignocellulosic material, which directly converted into panel boards without using any synthentic adhesives. Mobarak *et al.*[4] discussed the self-bonding capacity of bagasse and bagasse pith when hot-pressed under varying conditions. Zu-shan and Paszner[6] demonstrated the feasibility of direct use of corncob powder as an adhesive resource. Later on, Okamoto *et al.*[7] reported the medium density fiberboard (MDF) binderless boards made from mixed softwood and hardwood fibers using steam-injection pressing. Ellis and Paszner[8] discussed the self-bonding potential of

various high hemicelluloses-content lignocellulosic materials in particleboards. More recently, Laemsak *et al.*[9] used steam-exploded fibers of oil palm frond for manufacturing binderless board, while Velasquez *et al.*[10-11] developed binderless fiberboard from steam-exploded *Miscanthus sinensis*. The pretreatment conditions and the pressing conditions that optimize the physico-mechanical responses of *Miscanthus sinensis* binderless fiberboards were also determined.[12] Angles *et al.*[13] studied the effects of pres-treatment severity and lignin addition in the softwood binderless panels. Xu *et al.*[14-15] reported on the mechanical properties of kenaf core binderless particleboards, such as sound absorption and thermal resistant. The possibility of producing binderless board from finely ground powder of kenaf core has also been investigated.[16]

Based on those researches, it showed that non-wood lignocellulosic materials were potential raw materials for binderless boards. Considering that no synthetic adhesive was applied, the bonding performance of binderless boards was greatly affected by the chemical changes of materials during manufacturing process. Effects of the steam/heat treatments depend on many variables, such as pressing time, temperature, moisture content, chemical composition of the lignocellulosics, and possibly many other factors that are still not yet understood. No papers deal with the relationship between chemical changes of binderless boards and their bonding performance has not been reported so far.

1.2 Chemical reactions during steam/heat treatments

It was well known that wood/non-wood based fragments could be converted into boards by steam/heat treatments without using any adhesive.[2] This phenomenon, called self-bonding, is improved by activating chemical components of the board constituents during steam/heat treatments. There are many possibly reactions taking place during steam/heat treatments. These reactions can be summarized as follows:[17] degradation of

both the hemicelluloses and part of the cellulose to produce simple sugars and other decomposition products[2,3,17]; thermal softening of the cell wall matrix[18]; crosslinking between carbohydrate polymers and lignin[19]; and an increase in cellulose crystallinity.[20-22] Regarding the nature of the linkages formed during treatment, it is still unclear whether hydrogen bond or covalent bond plays an important role in the self-bonding. Wellons and Krahmer[23] supposed that thermoplastic flow and physical consolidation of cork particles at temperature below 205 °C were the main factor in bonding. However, eventhough some literatures have supported one or more of the above theories, the mechanism of self-bonding during steam/heat treatment has not been completely elucidated so far.

Another approach to wood bonding systems involves bonding without adhesives by chemically activating the wood surfaces. A number of activating chemicals have been used successfully to induce the chemical bonding.[24] Activation by nitric acid appeared to produce the most consistent results.[25] Lignin and xylan (hemicelluloses) were extensively modified components. Important aspects of nitric activation of wood surfaces were oxidation, nitration and also hydrolysis of wood polymers.[24-27] Another activators which provided good mechanical and physical properties of bonded products was hydrogen peroxide.[28] Recently, Rowell *et al.*[17] reported that the addition of ferric chloride to the process, as catalyst, reduced the hemicelluloses content of aspen fiberboards and greatly increased dimensional stability. Hasan *et al.*[29] showed that mechanical properties of esterified bagasse composite were enchanced with increasing monoester contents.

Basically, it was believed that degradation of hemicelluloses during steam/heat treatments was believed to play an important role in the self-bonding of binderless boards.[2] Therefore, the binderless boards usually used non-woody materials as raw materials, which is rich in hemicelluloses.[2-4,6,8-12,14-16] Shen had developed and patented a steam-explotion process of binderless boards.[2] He claimed that furan monomers were

formed in the process. Ellis and Paszner[8] reported that the bonding strength was directly proportional to the pentosan content of the raw material used. Suzuki *et al.*[19] suggested that released lignin and furfural derivatives generated during steam explosion contribute to self-bonding of the steam-exploded pulps. They found that severe steam-explosion condition caused great damage in lignin macromolecules and gave poor quality of binderless boards.

Steam treatment has been known to be effective method for improving the dimensional stability of wood based composites.[30-33] In the resin bonded boards, steam-injection pressing not only treats the woods but also affects the curing of adhesive resin as well. Hse *et al.*[34] found that in phenol formaldehyde and melamine urea formaldehyde resin systems, steam-injection pressing resulted in higher dimensional stability and lower bond strength than conventional platen pressing. The same effect of steam treatment was found on the dimensional stability of binderless boards. Okamoto *et al.*[7] reported that the dimensional stability of the MDF binderless boards made from mixed softwood and hardwood fibers could be improved by using steam-injection pressing. Rowell *et al.*[17] showed that high temperature steam treatment (200 °C) of wood fiber greatly increased the dimensional stability and decreased the hemicelluloses content of the binderless boards. It was also found that dimensional stability of steam-pressed binderless particleboard from kenaf core were better than hot-pressed boards.[14-15]

1.3 Characteristic of non-wood lignocellulosic materials

Non-wood lignocellulosic materials have been considered to produce various composite products. These resources are abundantly available in many countries; including residues from annual growth plants.[35] Most of non-wood lignocellulosic materials have very low densities, which make them extremely bulky. The collection,

transportation and storage of these materials call for special attention, due to the bulky nature of bagasse, cereal straw, etc. High compaction ratio and transport costs were one of the restrictions for utilization of bulk densities materials.

Generally, physical and chemical characteristic and structures of non-wood lignocellulosic materials are different from those of wood. Sugarcane bagasse, cereal straws, and corn stalks are more similar to hardwoods as the "fiber" fraction is in the same order; however, they are much more heterogeneous and contain a large proportion of very thin-walled cells and fine epidermal cells in a wide range of dimensions.[36-37] Kenaf, flax straw, and hemp contain two distinct fiber types: an inner core of short fibers surrounded by a layer of longer bast fibers. Core fibers typically contain more lignin and are more difficult to pulp.[36-37]

Table 1.1 shows the chemical properties of some common non-wood lignocellulosic materials. [36-37] Non-woods are usually characterized by a lower lignin content and a higher pentosan/hemicelluloses content than softwood. These materials seemed to be potential raw materials for manufacturing binderless boards, considering that degradation of hemicelluloses during steam/heat treatment is believed to play an important role in the self-bonding formation.

Chemical composition varies from plant to plant, and within diferent parts of the same plants. It also varies within plants from different geographic locations, ages, climate, and soil conditions.[38-42] Stalk fibers are closer to hardwoods in chemical properties than to softwoods, which the major difference is in the higher ash and silica content of these nonwoods. Fibers from straw and bagasse are short and limit the range of paper qualities that can be produced.[36]

Table 1.1 Chemical properties of various non-woods (Huther, 1997)

Fiber Source		Cross & Bevan Cellulose (%)	α-Cellulose (%)	Lignin (%)	Pentosans (%)	Ash (%)	Silica (%)
Bast Fibers							
Jute		57 - 58	39 - 42	21 - 26	18 - 21	0.5 - 1	<1
Jute sticks (whole jute)			43				
Kenaf - bast		47 - 57	31 - 39	7.5 - 9.5	16 - 23	2 - 5.5	
Kenaf - core			34	17.5	19.3	2.5	
Oilseed flax tow		47	34	23	25	2 - 5	
Textile flax tow		76 - 79	50 - 68	10 - 15	6 - 17	2 - 5	<1
Leaf Fibers							
Abaca		78	61	9	17	1	<1
Sisal		55 - 73	43 - 56	8 - 9	21 - 24	0.6 - 1	<1
Seed Hull Fibers							
Cotton staple			85 - 90	3 - 3.3		1 - 1.5	<1
Cotton linters			80 - 85	3 - 3.5		1 - 1.2	<1
Stalk Fibers							
Canes	sugarcane bagasse	49 - 62	32 - 44	19 - 24	27 - 32	1.5 - 5	0.7 - 3
	bamboo	57 - 66	26 - 43	21 - 31	15 - 26	1.7 - 5	1.5 - 3
Cereal aw	barley	47 - 48	31 - 34	14 - 15	24 - 29	5 - 7	3 - 6
	oat	44 - 53	31 - 37	16 - 19	27 - 38	6 - 8	4 - 7
	rice	43 - 49	28 - 36	12 - 16	23 - 28	15 - 20	9 - 14
	rye	50 - 54	33 - 35	16 - 19	27 - 30	2 - 5	0.5 - 4
	wheat	49 - 54	29 - 35	16 - 21	26 - 32	4 - 9	3 - 7
Grasses	arundo donax		29 - 33	21	28 - 32	4 - 6	1.1 - 1.3
	esparto	50 - 54	33 - 38	17 - 19	27 - 32	6 - 8	2 - 3
	sabai	54 - 57		17 - 22	18 - 24	5 - 7	3 - 4
	switchgrass		43	34 - 36	22 - 24	1.5 - 2	
Reeds	phragmites mmunis	57	45	22	20	3	2
Woods							
Coniferous (softwood)		53 - 62	40 - 45	26 - 34	7 - 14	1	<1
Deciduous (hardwood)		54 - 61	38 - 49	23 - 30	19 - 26	1	<1

In the tree, lignins have been found to interact with the polysaccharides, particulary hemicelluloses, with which they coexist, leading to formation of another chemical component, a kind of glycoconjugate.[43] There are several types of lignin-carbohydrate linkage have been proposed such as benzyl ester type, benzyl ether type, glycosidic type, and acetal type.[43] Among of these chemical linkages, the benzyl ether and ester types have been considered to be most probable mode of linkage.

It was also well known that grasses had substansial amounts of hydroxycinnamic acids intimely associated with the cell wall.[44-48] Cell walls of grasses compose of hydroxycinnamic acids, such as *p*-coumaric and ferulic acids.[46] These hydroxycinnamic acids (Fig.1.1) are two reactive functional groups, -COOH and phenolic OH groups, suggesting the presence of ester-ether bridges between lignin and polysaccharides through hydroxycinnamic acids and their derivatives.[45] Lam *et al.*[46] analyzed ester-ether linked of cinnamic acids in grasses and reported that the benzyl ether bond participates in ferulic and diferulic acid bridges between lignin and polysaccharides in grass cell walls.

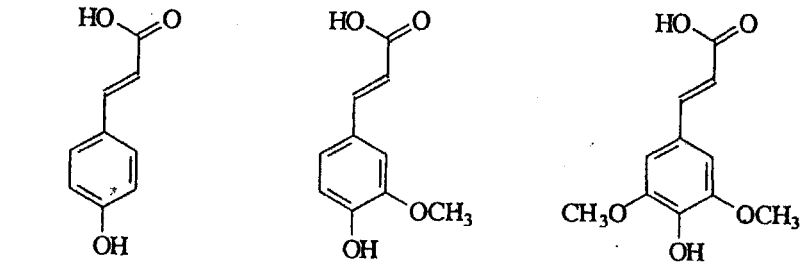

Fig 1.1 Hydroxycinnamic acids

Lam *et al.*[46] found that cinnamic acids groups in wheat lignin were bound to polysaccharides by ester linkages. Morison *et al.*[39] reported low content of ester-linked and ether-linked hydroxycinnamic acids at bottom core of kenaf, being considered to be

mostly ester-linked to some portion of cell walls. Sun *et al.*[49] concluded that *p*-coumaric acid at bagasse lignin was linked to lignin by ester bond, whereas ferulic acid was linked to lignin by both ester and ether bonds. Figure 1.2 shows the ferulate has a role in cross-linking polysaccharides with lignin.[47]

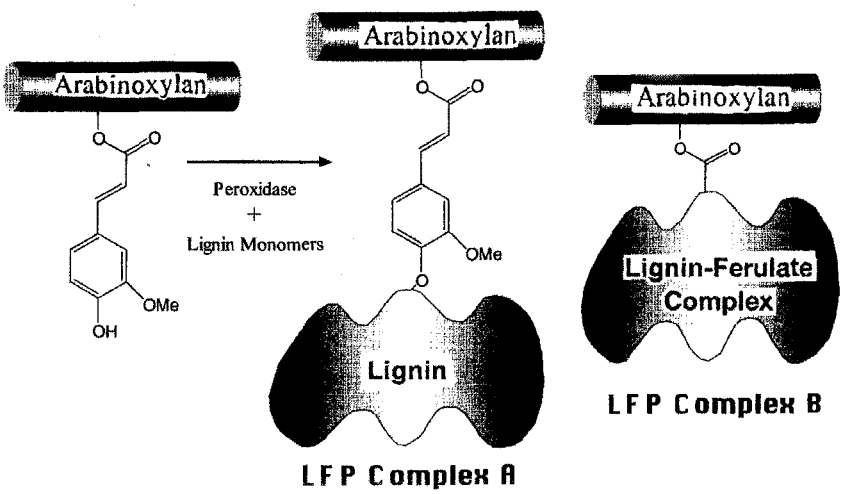

Fig 1.2 Ferulates, exported into cell wall region as esters of polysaccharides, (primarily arabinoxylans in grasses), will cross-link with lignin via 2 mechanisms to yield a cross-linked lignin-ferulate-polysaccharide (LFP) complex from which the ferulate may releasable (LFP complex A) and may not releasable (LFP complex B). (Ralph *et al.*, 1998)

1.4 Objectives of study

Non-wood lignocellulosic materials are potential raw materials for binderless boards production Studies on manufacturing process of binderless board have been conducted for years. However, the self-bonding mechanism during steam and heat treatments has not been completely elucidated so far.

The objective of this study is to investigate the chemical changes of non-wood lignocellulosic material during steam-injection pressing and hot-pressing treatments, in order to characterize the self-bonding of binderless board. Considering the chemical characteristics of non-wood materials are different from those of wood, it is also necessary to discuss the role of cinnamic acids during steam and heat treatments. In this study, kenaf core and bagasse were used as raw materials of binderless particleboard.

The present paper consists of four chapters;

1. Chapter 1 deals with literature reviews on the subject covering the development of binderless board, chemical reactions during steam/heat treatments, and characteristic of non-wood lignocellulosic materials.
2. Chapter 2 describes on the chemical changes of kenaf core during steam/heat treatments. Effects of steaming conditions and pressing methods on the chemical degradation are discussed. Furthermore, relationship between chemical changes and internal bond strength/ thickness swelling of binderless boards are also studied.
3. Chapter 3 presents the self-bonding characterization of kenaf core composites. First, the optimization of steaming condition for bonding strength of kenaf core composites is investigated. To discuss the role of cinnamic acids during steam treatment, analysis using pyrolysis gas chromatography mass spectrometry in the presence of methylation agent is used.
4. Chapter 4 deals with the physical and chemical properties of bagasse binderless boards. Effects of material type, pressing condition and storage methods on the mechanical and chemical properties of binderless boards are investigated. Furthermore, the self-bonding mechanism of non-wood materials is discussed.

CHAPTER 2

CHEMICAL CHANGES OF KENAF CORE DURING STEAM/HEAT TREATMENTS

2.1 Introduction

Kenaf (*Hibiscus cannabicus L.*) is one of the fast growing annual plants. The stalk consists of an outer bast layer and an inner core. The core comprises roughly 60% dry weight of kenaf stalk, and it is extremely light in weight, with a density of 100-200 kg/m^3, which is a potential material for low-density boards.[50-51] In addition, kenaf core is rich in hemicelluloses, which are necessary for binderless board manufacturing.[14-15,50]

It was discussed in the chapter 1 that steam treatment was an effective method for improving the dimensional stability of wood based composites. Okamoto *et al.*[7] showed that steam-injection pressing improved the dimensional stability of the binderless MDF made from mixed softwood and hardwood fibers, although the internal bonding (IB) was very low. Hsu *et al.*[52] reported that dimensionally stable wood-based composite was made from steam treated furnish (at 1.55 MPa for 3-4 min) if the total content of water-insoluble xylan, mannan and galactan of pine and aspen were reduced to about less than 15.5 % and 16.5 %, respectively.

Xu *et al.*[14-15] developed binderless particleboards from kenaf core using steam-injection pressing. The IB strength of these boards was relatively excellent, although low steam pressure of 0.6 – 1.0 MPa was used. The thickness swelling (TS) of binderless boards was greatly affected by steam-injection pressing. Significant differences of mechanical properties between steam-pressed and hot-pressed binderless boards were also clearly found. Being considered there was no adhesive used, the bonding performance and dimensional stability of the kenaf core binderless particleboards was suggested greatly

affected by chemical changes of components during steam/heat treatments. It was mentioned in chapter 1, the mechanism of self-bonding during steam and heat treatment has not been completely elucidated so far. In addition, no papers deal with the relationship between chemical changes of boards and their bonding performance has not been reported.

This chapter is designed to investigate the chemical changes of kenaf core binderless board manufactured by steam-injection pressing and hot pressing treatment. Kenaf core and its binderless boards are analyzed for its extractives, holocellulose, cellulose, and lignin. The neutral sugar composition of the water–soluble fraction is determined using an alditol-acetate method, while kenaf lignin is analyzed using pyrolysis coupled to gas-chromatography-mass spectrometry (Py-GC-MS). Furthermore, the effects of chemical changes on the self-bonding performance and dimensional stability of particleboards are discussed.

2.2 Materials and Methods

2.2.1 Materials

Kenaf core variety Chinpi-3 (*Hibiscus cannabicus L.*) binderless particleboards were used as the raw materials for chemical analyses.[14] Boards were prepared by steam-injection pressing under the following conditions: 1 MPa (183 °C) for 7 min, 10 min, 15 min, and 20 min; 0.8 MPa (175 °C) and 0.6 MPa (164 °C) for 20 min. Boards prepared by hot pressing system were subjected to 190 °C for 20 min. The target density of all binderless boards was 0.55 g/cm^3. All of boards and kenaf core (as control) were cut and ground to pass through 30 mesh screen, were retained on 60 mesh screen, and were then air dried. Figure 2.1 shows the scheme of chemical analysis of kenaf core and its binderless boards.

2.2.2 Chemical analysis of kenaf core and the binderless boards

The kenaf core samples were extracted successively with a mixture of ethanol and benzene (1:2, v/v) for 24 h by refluxing, and then with distilled water at 60 °C for 3 h. The analyses of extractives were carried out in duplicates. The water-soluble fraction from the samples was then subjected to analyses of neutral sugar composition and ^{13}C-nuclear magnetic resonance (^{13}C-NMR). Lignin and acid-soluble lignin were determined by a Klason method. Holocellulose content was analyzed by a Wise method. The α-cellulose content was determined using the holocellulose by extraction with 17.5% NaOH. All the chemical analyses were carried out in triplicate.

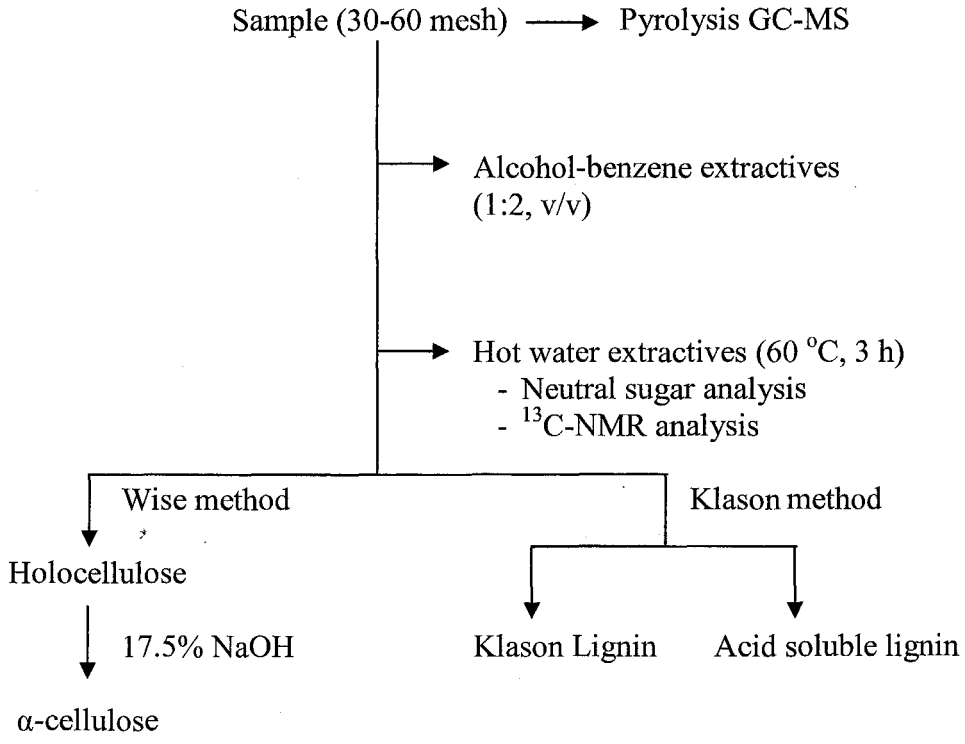

Fig.2.1 Scheme of chemical analysis of kenaf core and its binderless boards

2.2.3 Analysis of water-soluble polysaccharides

The water-soluble fraction was analyzed by ^{13}C-NMR. The spectra were measured on a JEOL λ-400 NMR spectrometer (Tokyo, Japan) at 100 MHz in D_2O at 27 °C using 1,4-dioxane as an internal standard (67.40 ppm).

The neutral sugar composition of the water-soluble fraction was determined as an alditol acetate by a gas chromatography (Shimadzu GC-17A, Shimadzu, Kyoto, Japan) on an ULBON HR-SS10 (0.25 mm x 25 m, Ulbon, Kyoto, Japan) after acid hydrolysis. The acid hydrolysis was carried out with trifluoroacetic acid (TFA) at 100 °C for 3 h. The column oven temperature was programmed to increase from 30 °C to 210 °C at a rate of 4 °C/min. All analyses were run in duplicate.

2.2.4 Analytical pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS)

Each sample (1 mg ± 0.1 mg) was analyzed by double shot pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) on a Shimadzu GCMS-QP5050A mass spectrometer equipped with a Frontier Lab Double-shot Pyrolyser PY-2020D (Fukushima, Japan). Separation of compounds was achieved on a fused silica capillary column, CP-Sil 8 CB (50 m × 0.25 mm i.d., Chrompack, Netherlands) using helium carrier gas. The temperatures of the injection port and separator were 280 °C. Double-shot pyrograms were obtained using a two-step temperature program. For the first shot, the temperature of the pyrolyzer was maintained at 50 °C for 1 minute, and then raised to 250 °C at a rate of 8 °C/min and maintained for 1 min. The programming of the column oven temperature for GC-MS was synchronized with the temperature program of the pyrolyzer. The column oven temperature for GC-MS was first maintained at 50 °C for 1 min, and then raised to 280 °C at a rate of 5 °C/min and maintained for 10 min. After the first shot, the column oven was cooled to 50 °C. Pyrolysis was carried out by dropping the sample holder into a pyrolysis port that had been heated to 500 °C. The pyrolysis was conducted for 1 min.

Pyrograms were obtained by GC-MS with the same temperature program described for the analysis of volatile compounds. All analyses were run in duplicate.

2.3 Results and Discussion

2.3.1 Chemical composition of binderless boards

Effects of steam pressure on chemical composition of the kenaf core binderless boards are shown in Figure 2.2. Amount of the alchohol-benzene and hot water extractives increased with increasing the steam pressure. Hot pressing treatments caused no significant effects on the amount of these extractives. When boards were treated by steaming at 1 MPa or by hot press for 20 min, it was found that the amount of hot water extractives from the steam-pressed boards increased up to 8.2%, while those of the hot-pressed boards remained at around 2.5%. In the steam treatments, the amount of the alcohol-benzene and hot water extractives increased with increasing pressing time, as shown in Figure 2.3. Hsu *et al.*[52] reported that the amount of water-soluble materials extracted from aspen and lodgepole pine after steam pretreatments at 1.55 MPa for 4 min increased from 2.1 % to 16.8 and 14.8%, respectively, based on the dry-weight of the material.

Figures 2.2 and 2.3 show that hemicelluloses, Klason lignin, acid-soluble lignin and α-cellulose also decreased with increasing the steam pressure and the pressing time. It showed that all of the major chemical components of kenaf core were degraded by steaming and contributed to the self-bonding. The effect of steam treatment was more marked than that of the hot pressing on the changes of chemical composition of boards.

Hsu *et al.*[52] found that under steam pretreatment at 1.55 MPa for 1-4 min, only the hemicelluloses of hardwood and softwood decreased, while lignin and cellulose content did not decrease significantly with increasing treatment time. Okamoto *et al.*[7] used steam

pressing in a pressure range of 0.6 – 1.1 MPa for 5 min to produce dimensional stable MDF. Under these conditions, hemicelluloses and cellulose decreased with increasing steam treatment, while the lignin component did not change significantly.[7]

It has been reported that steam plays an important role in chemical reactions such as formation of acetic acid and hydrolytic cleavage of glycosidic bonds in polysaccharide chains.[8] Lignin was more resistant to the steam treatments than hemicelluloses but some components of lignin were gradually degraded or modified by steaming.[53] Yap[54] reported that the effectiveness of autohydrolysis was realted to extent of lignin content in the wood. Suchsland *et al.*[55-56] found that increasing steam pressure caused increase in finest content of the furnish, which seemed to be responsible for the improvement of board properties.

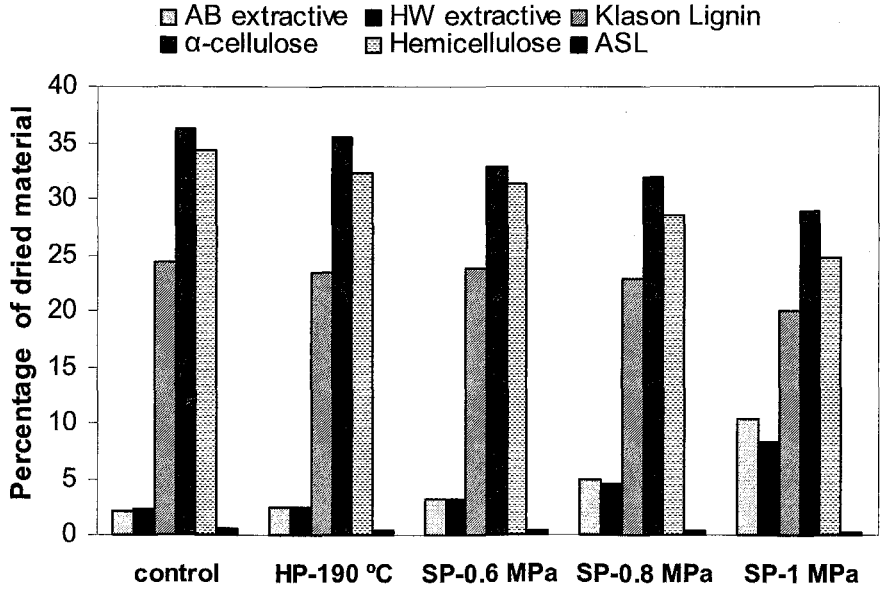

Fig. 2.2 The effect of steam pressure on chemical composition of binderless boards. Pressing time was 20 min, corrected board density was 0.5 g/cm^3. AB, alcohol-benzene; HW, hot water; ASL, acid soluble lignin; HP, hot-pressed board; SP, steam-pressed board

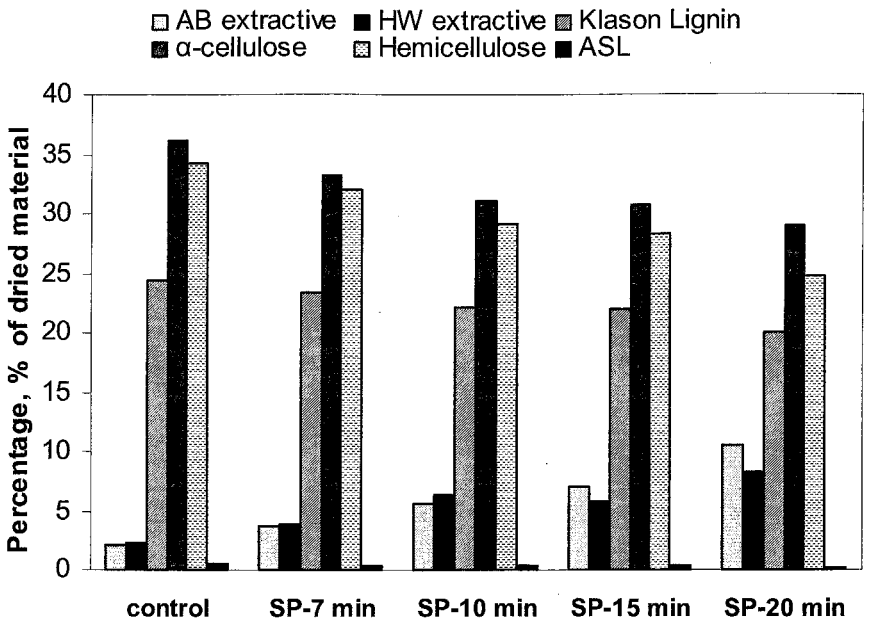

Fig. 2.3 The effect of pressing time on chemical composition of binderless boards. Steam pressure was 1 MPa, corrected board density was 0.5 g/cm^3. AB, alcohol-benzene; HW, hot water; ASL, acid soluble lignin; HP, hot-pressed board; SP, steam-pressed board

The color of the steam-treated binderless boards from kenaf core was dark brown and became darker with increasing the steam pressure and pressing time. This indicates that a high degree of hydrolysis or modification of the chemical component occurred during the steam treatment. Hemicelluloses are hydrolyzed to increase their solubility in water during the steam/heat treatment. Water-soluble components are mainly derived from the hemicelluloses degradation products.[66]

Low-pressure steam treatment was found to have a large effect on the changes in chemical composition of kenaf core binderless boards. Kenaf core contains hemicelluloses such as glucuronoxylan and glucomannan.[40,41] Lignin is deposited in the cell walls in

association with the hemicelluloses via different types of covalent linkages. Morison *et al.*[39] reported low content of ester-linked and ether-linked hydroxy-cinnamic acid (*p*-coumaric acid and ferulic acid) in the bottom core of kenaf, being considered to be mostly ester-linked to some portion of cell walls. Ester linkages, which are alkaline-labile linkage, are also susceptible to the hydrolysis during the steam/heat treatments. Arabinofuranosyl residues in glucuronoxylan also participate in the lignin-carbohydrate bonds through cinnamic acid residues, *p*-ferulic and *p*-coumaric acids.

2.3.2 Analysis of water-soluble polysaccharide

Analysis of water-soluble polysaccharide by ^{13}C-NMR (Fig. 2.4) showed that hemicelluloses of kenaf core mainly consist of 4-*O*-methyl-glucuronoxylan and a small amount of glucomannan, as reported by Neto *et al.*[40] and Ohtani *et al.*[41] The presence of glucuronoxylan in kenaf has also been confirmed by Das *et al.*[57] A part of the glucuronic acids attached to the xylan backbone are linked with lignin by ester bonds.

The neutral sugar composition of water-soluble polysaccharide from kenaf core and their binderless boards is shown in Table 2.1. Hemicelluloses were hydrolyzed to increase their solubility in water, while cellulose was resistant to hydrolysis during steam treatments. The results demonstrated that xylose content increased with increasing steam pressure. The amount of xylose in the hot water extract of the kenaf boards after steam treatment at 1 MPa for 20 min was 3.0%, based on the dry-weight of the kenaf boards, while that obtained after hot pressing at 190 °C for 20 min was 0.05%. Thus, marked differences were found in the amount of soluble xylan between the steam and hot press treatments.

Figure 2.4 ^{13}C-NMR spectrum of water-soluble polysaccharides from steam-pressed kenaf core binderless board treated at 1 MPa for 20 min. The spectrum was obtained at 100 MHz at 27 °C in D_2O solutions. Asterisk, unidentified component

Table 2.1 Neutral sugar composition of water-soluble polysaccharide

	Rhamnose	Arabinose	Xylose	Mannose	Galactose	Glucose
Control	0.02	0.01	0.03	0.04	0.02	0.09
HP (190 °C)	0.03	0.04	0.05	0.05	0.02	0.08
SP-0.6MPa	0.04	0.02	0.14	0.03	0.03	0.24
SP-0.8MPa	0.09	0.04	0.99	0.10	0.10	0.29
SP-1.0MPa	0.05	0.03	2.98	0.12	0.12	0.30

Sugar composition as percentage based on dry weight of material

HP, hot-pressed board; SP, steam-injection pressed board

Hsu *et al.*[52] reported that xylose content in a hot water extract from aspen treated by steam at 1.55 MPa for 4 min was 0.35%. Compared with this result, the glucuronoxylan in kenaf appears more susceptible to hydrolysis by steam than aspen wood. The differences in the effects of solubilization of xylose can be explained by the network of lignin-glucuronoxylan complexes involving *p*-cinnamic acid bridges in kenaf core.

2.3.3 Pyrolysis GC/MS analysis

The pyrograms of kenaf core is shown in Figure 2.5, and the syringyl/guaiacyl (S/G) ratios are shown in Table 2.2. Kenaf core is composed of lignin with guaiacyl, syringyl and *p*-hydroxyl nuclei. The S/G ratio from this experiment was calculated to be 2.1 for the kenaf core. This is consistent with the values of previous report, 1.2 - 2.2 for the S/G ratios for kenaf core.[39,41-42,58]

The S/G ratio decreased with increasing pressure of steam treatment. The S/G ratios of binderless boards treated by steaming at 0.6, 0.8 and 1 MPa for 20 min were 2.0, 1.9 and 1.7, respectively. This indicated that substructures containing S units were preferentially

decomposed by the steam treatment over those containing G units due to the more highly condensed structures of the G units than those of the S units.

In contrast to the effects of steam treatment, a S/G ratio in the hot pressed kenaf boards was found to be close to that of original kenaf core, demonstrating that chemical modification of lignin by hot pressing is not as marked as that observed in the steam treatment, although a slight decrease in Klason lignin by hot pressing was found. In the manufacture of binderless boards from oil palm fronds, decreasing S/G ratio was observed in both steam explosion and hot pressing process.[19] The ratio S/G was considered to have the most significant effect on the removal of lignin in cell walls.[59]

2.3.4 Bonding strength and thickness swelling of binderless boards

Because adhesives were not used in the binderless boards, self-bonding strength was significantly affected by the changes in chemical composition of the boards caused by the steam/heat treatments. Correlation between chemical composition and internal bond (IB) strength of the binderless boards is shown in Fig. 2.6. IB strength increased with increased amount of hot-water extract and reached a plateau when the amount of hot water extract reached twice that of the untreated boards. Similar correlation was found between the IB strength and the extent of hemicelluloses, lignin and cellulose degradation. It seemed that degradation of the three chemical components by steam pressing increased thermoplastisity, leading to deformation to a stable matrix.

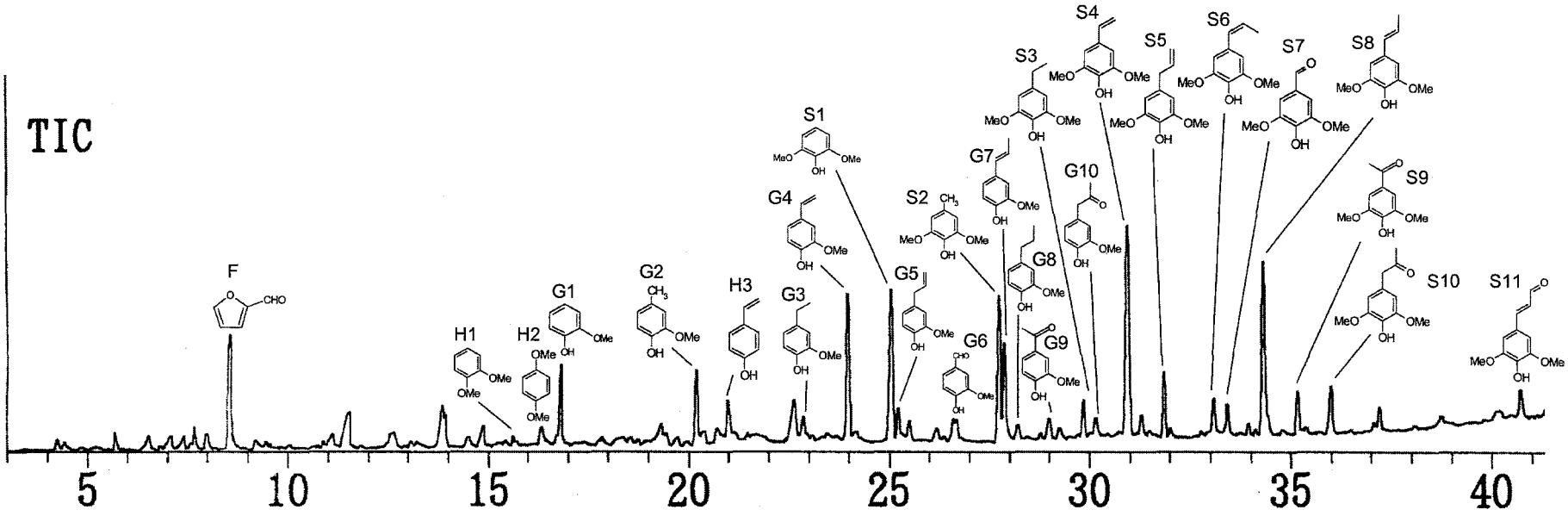

Fig.2.5 Products of kenaf core pyrolyzed at 500 °C for 1 min

Table 2.2 Ratio of S/G of the boards by pyrolysis GC/MS*)

		Control	HP 190 °C 20 min	SP 1 0.6 MPa 20 min	SP 6 0.8 MPa 20 min	SP 8 1 MPa 7 min	SP 7 1 MPa 10 min	SP 9 1 MPa 15 min	SP 10 1 MPa 20 min
G1	Guaiacol	5.6	5.1	6.7	6.9	6.6	6.9	7.1	7.8
G2	4-methylguaiacol	4.1	4.2	3.9	3.9	4.6	4.5	4.9	5.2
G3	4-ethylguaiacol	0.7	1.6	2.2	4.3	1.4	6.7	6.8	4.9
G4	4-vinylguaiacol	9.6	8.7	8.6	8.2	9.6	8.4	8.8	8.9
G5	Eugenol	1.9	1.8	1.7	1.9	1.9	1.2	1.4	1.2
G6	Vanillin	1.3	2.0	2.2	1.7	1.8	1.9	1.7	1.3
G7	Isoeugenol	5.3	4.9	4.7	4.2	5.0	3.5	4.0	4.2
G8	4-propylguaiacol	1.2	1.4	1.1	1.0	1.1	1.0	1.0	0.9
G9	Acetoguaiacone	1.5	1.5	1.2	1.1	1.1	1.3	1.0	1.1
G10	Guaiacylacetone	1.3	1.2	1.7	1.5	1.8	1.4	1.3	1.1
		32.5	32.4	33.9	34.7	34.7	36.6	37.9	36.6
S1	Syringol	10.8	10.6	10.8	11.5	10.6	11.3	11.9	13.2
S2	4-methylsyringol	8.8	9.3	9.2	9.2	8.8	9.5	9.3	10.0
S3	4-ethylsyringol	1.6	1.8	1.7	1.6	1.5	1.7	1.6	1.7
S4	4-vinylsyringol	19.8	17.8	17.5	17.1	17.7	16.5	14.5	13.4
S5	4-allylsyringol	3.4	3.2	3.4	3.5	3.3	2.2	2.9	4.2
S6	4-propenylsyringol (*cis*)	2.4	2.4	2.1	1.8	2.1	2.0	2.4	2.2
S7	Syringaldehyde	3.7	3.6	3.4	2.8	3.4	3.2	3.1	2.9
S8	4-propenylsyringol (*trans*)	10.6	11.8	12.0	12.1	11.9	11.6	11.4	10.6
S9	Acetosyringone	2.3	2.5	2.2	2.1	2.1	2.0	1.7	1.9
S10	Syringylacetone	2.4	2.6	2.5	2.7	2.3	2.5	2.3	2.8
S11	Sinapaldehyde	1.6	2.1	1.3	1.1	1.6	0.7	1.0	0.4
		67.5	67.6	66.1	65.3	65.3	63.4	62.1	63.4
	Ratio S/G	2.1	2.1	2.0	1.9	1.9	1.7	1.6	1.7

*)as relative percentage of total-ion areas of pyrolysis products originated from lignin
S, syringyl; G, guaiacyl; HP, hot-pressed board; SP, steam-pressed boar

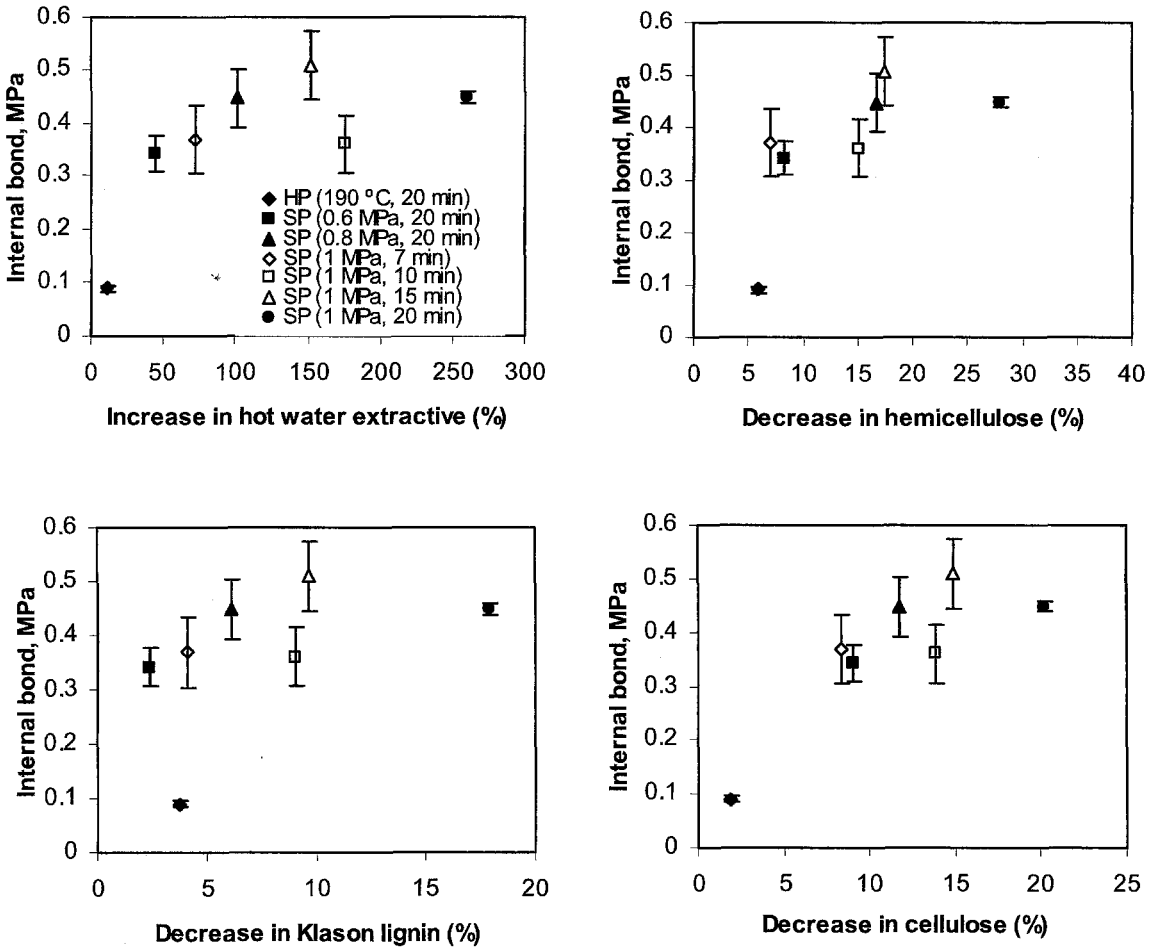

Fig. 2.6 The effect of chemical changes by steam/heat treatment on internal bond strength of binderless boards. The corrected density of binderless boards was 0.5 g/cm^3. HP, hot pressing; SP, steam-injection pressing.

Cellulose gives mechanical strength to plant tissues while lignin provides rigidity and stiffness. Therefore, it is well known that intensive degradation of hemicelluloses, lignin and cellulose decrease physical quality of the boards. Suzuki *et al.*[19] reported that steam explosion of oil palm frond fiber at 3 MPa produced boards of poor quality. In this study, low steam pressure (0.6-1.0 MPa) was applied. Nevertheless, compared with other binderless boards,[7,9] kenaf core binderless particleboards showed higher bondability.

It should be noted that hot pressing with the lowest degradation of the cell wall components gave the lowest IB strength of the board (about 0.09 MPa). Differences in the manufacturing process showed a significant effect on the bonding properties. In hot pressing, steam was generated from moisture in kenaf core particles during processing. By injecting high-pressure steam, the temperature of binderless boards would rise immediately; therefore it seemed that the chemical components would degrade, polymerize and arrange a stable network in a short time range during the treatment. This effect was not obtained by hot pressing, which degraded the chemical components of kenaf much less effectively.

In the resin-bonded boards, the thickness swelling (TS) values depend on the potential thickness recovery of densified particles and breakage of the adhesive bond network.[30] Because no adhesives were used in the boards, the TS values would depend on the chemical behaviors of particle during treatment. The reduction in hygroscopicity, which because of the changes in hemicelluloses, was one main reason of improved dimensional stability.[11,30,60] The same results are shown in Fig. 2.7. However, the reduction of the TS values of binderless boards was also strongly related to the decrease of lignin and cellulose contents of boards during steam treatment. These facts showed that the degradation of chemical components by the steam/heat treatment to a certain degree increased the compressibility of boards and reduced the internal stress induced in each particle. In the

present study, the TS decreased significantly by using steam-injection pressing. With a steam pressure of 1 MPa, the mean TS value was 7.47% for a 20-min treatment, whereas the mean TS value of hot pressed boards at 190 °C was 169%. It showed that steam treatment could improve the dimensional stability of boards, as can also be found in other papers.[30-33]

2.4. Summary

In the manufacturing of kenaf core binderless boards by steam-injection pressing, not only hemicelluloses, but lignin and α-cellulose also contributed to self-bonding. Based on dry weight of materias, the decrease of hemicelluloses (up to about 28%), α-cellulose (up to about 20%), lignin (up to about 18%) and increasing of water-soluble fractions (up to about 260%) by steam-injection pressing (0.6 – 1.0 MPa) could produce kenaf core binderless boards with relatively good quality. Steam-injection pressing was an effective method to improve the bonding performance and dimensional stability of binderless boards. Hot pressing also caused degradation of chemical component, but not to a significant degree to improve their binding ability.

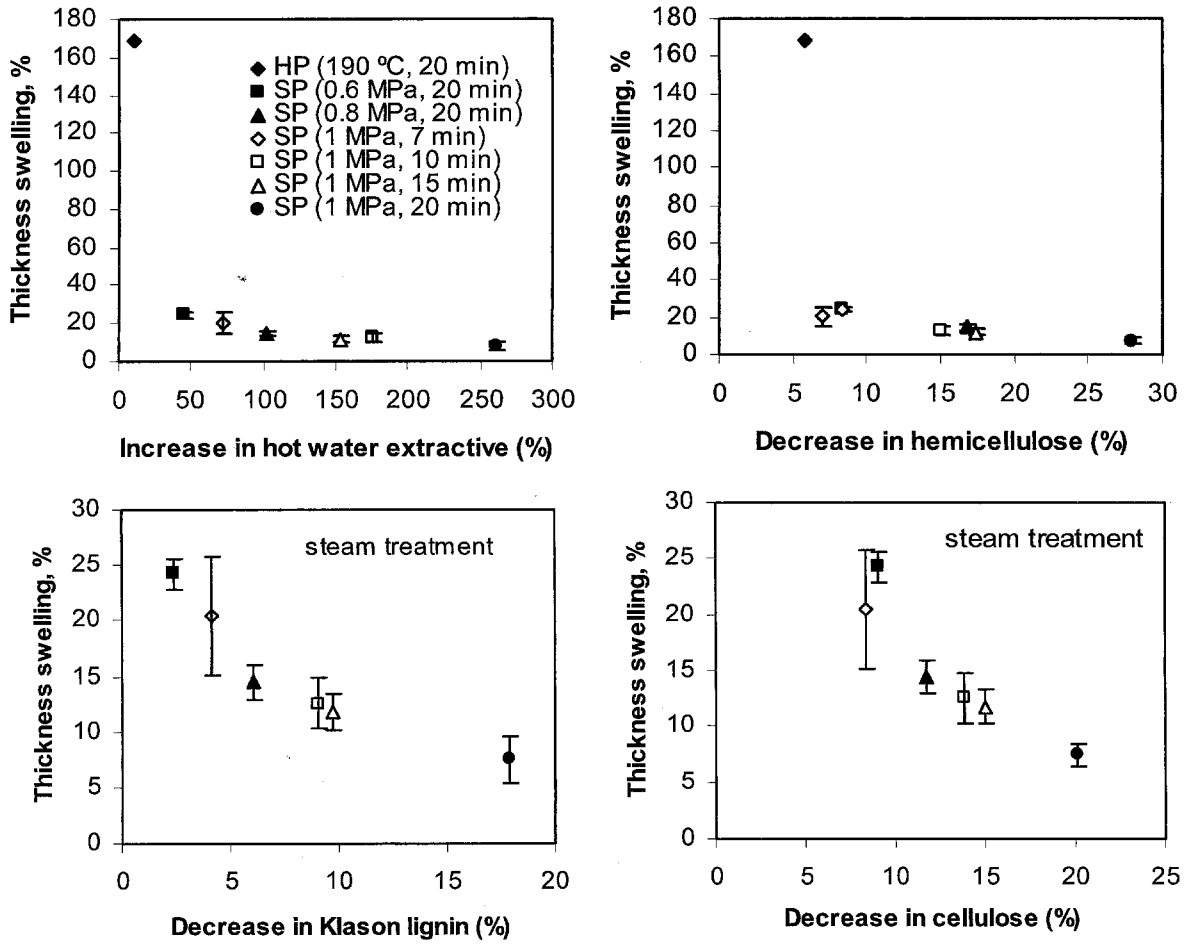

Fig. 2.7 The effect of chemical changes by steam/heat treatment on thickness swelling of binderless boards.

The corrected density of binderless boards was 0.5 g/cm^3. HP, hot pressing; SP, steam-injection pressing.

CHAPTER 3

BONDING CHARACTERISTICS OF BINDERLESS KENAF CORE COMPOSITES

3.1. Introduction

Kenaf core binderless particleboards were successfully manufactured by steam-injection treatment.[14-15] The results showed that the bonding properties of these binderless boards were relatively high compared with those of hot-pressing treatment or even other binderless boards,[7,9] at the same densities. It was also found that a partial degradation of three main major chemical components of the kenaf core by mild steam-injection treatment increased the bonding performance and dimensional stability of the binderless boards.[60]

It was well known that interactions between polysaccharides and lignin through cinnamic acids ester-ether bridges have been postulated for cell wall of grasses/non-wood lignocellulosic materials, such as kenaf.[44-48,61] Morison *et al.*[39] reported low content of ester-linked and ether-linked hydroxy-cinnamic acids (*p*-coumaric acid and ferulic acid) at bottom core of kenaf, being considered to be mostly ester-linked to some portion of cell walls. Ester linkages, known as alkali-labile linkages, are suggested susceptible to cleave during steam treatment due to the degradation of hemicelluloses and lignin. Therefore, the presence of cinnamic acids in the self-bonding mechanism of binderless board is interesting to be studied, considering that binderless boards are usually made from non-wood lignocellulosic materials. However, no papers concerned on the role of cinnamic acids during steam/heat treatments have been conducted.

In chapter 2, kenaf lignin was characterized using conventional pyrolysis, which could not identify the cinnamic acids. Therefore, in this study, kenaf core is analyzed by

pyrolysis-gas chromatography mass spectrometry with methylation agent using tetramethylammonium hydroxide (TMAH/Py-GC-MS). This method avoid the decarboxylation of polar moieties and yields phenolic derivatives, which are not observed during conventional analytical pyrolysis.[58,62-65]

This chapter is designed to investigate the optimum self-bonding conditions of kenaf core composites using steam treatment and to discuss the roles of cinnamic acids during steam treatment. Two plies of laminated kenaf core are treated by steam treatment under various conditions. The weight loss during steam treatment and the shear strength are then calculated. Furthermore, the lignin of untreated and steam-treated kenaf core is identified using TMAH/Py-GC-MS. In addition, the presence of cinnamic acids in the water-soluble fractions of steam-treated samples is also analyzed.

3.2. Materials and methods

3.2.1. Materials

Kenaf (*Hibiscus cannabinus L.*) core variety Chinpi-3 about 10-20mm in diameter was used as raw materials. Kenaf core was cut into dimensions 75 mm (L) x 10 mm (W) x 2 mm (T). The samples were then air dried to about 11% moisture content.

3.2.2. Steam treatment and bonding analysis

A pair of air-dried veneer sawn kenaf core was pressed using a special porous metal (Kobe Steel Co. Ltd., Japan) in the autoclave (see Figure 3.1) where high-pressure steam was injected under the following conditions: 1.5 MPa (200 °C) for 1 min, 3 min, 5 min, and 7 min; 1 MPa (183 °C) for 1 min, 3 min, 5 min, 10 min, 15 min, and 20 min; 0.8 MPa (175 °C) and 0.6 MPa (164 °C) for 10 min, 15 min, and 20 min. The compression speed was 10 mm/min and the thickness of distance bar was 2 mm. After steaming treatment, the

two-ply laminated kenaf core was conditioned (20 °C, 65% RH) until further analysis will be conducted. Four replicate runs were done for each condition.

Shear blocks test specimens were cut from each panel and were tested according to ASTM D-2339.[65] The weight loss was calculated by measuring the weight of samples before and after the steam treatment.

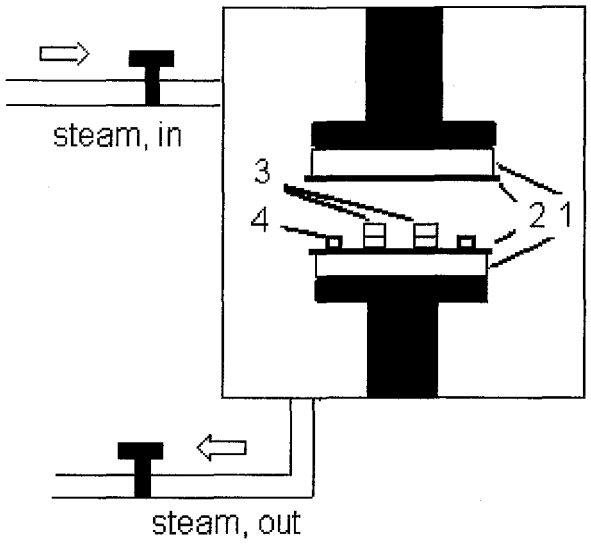

Fig.3.1 Apparatus for steam treatment. 1, porous metal; 2, teflon sheet; 3, sample; 4, distance bar (thickness: 2 mm).

Two sets of four samples of two-ply laminated kenaf core, which manufactured at the condition of 1 MPa for 10 min, were immersed in different conditions; in hot water at 70 °C for 3 h or in the cold water at 20 °C for 3 h. After immersed, the samples were cut and measured for their shear strength. These water-soluble fractions were condensed by vacuum evaporation and freeze-dried. The extractives were kept in the refrigerator for further analysis by TMAH/Py-GC-MS.

3.2.4. Analysis by tetra methylammonium hydroxide pyrolysis-gas chromatography-mass spectrometry (TMAH/Py-GC-MS)

Kenaf core (as control), steam-treated samples, and its extractives were analyzed by TMAH/Py-GC-MS. The sample (0.2 ± 0.01 mg) was placed on a 20 μm ferromagnetic pyrofoil. A solution of 1 mmol/ml 3-ethoxy-4-hydroxybenzaldehyde (Nacalai Tesque Inc., Kyoto, Japan) in methanol (1 μl) was added as internal standard (IS). Tetra methylammonium hydroxide (25% in methanol solution, Nacalai Tesque Inc., Kyoto, Japan) as methylating agent was dropped on the sample about 3 μl. Then, the mixture was air-dried for 30 min. The samples were pyrolyzed at 500 °C for 6 s. The pyrolysis was performed on a Shimadzu GCMS-QP5050A Mass Spectrometer (Kyoto, Japan) equipped with a Frontier Lab Pyrolyser PY-2020D (Fukushima, Japan). Separation of compounds was done on a fused silica capillary column, CP-Sil 8 CB (50 m × 0.25 mm i.d., Chrompack, Netherlands) using helium as a carrier gas (total flow rate, 27 ml/min). The temperatures of the injection and detector ports were kept at 280 °C. The programming of the column oven temperature for GC-MS was synchronized with the temperature program of the pyrolyzer. The column temperature for GC-MS was kept at 50 °C for 1 min, and then raised to 280 °C at a rate of 5 °C/min and after which was maintained for 10 min. Peak assignments were carried out by comparison of their mass spectra and relative retention time with those of authentic compounds and reference data.[50-54] TMAH/Py-GC-MS analysis was carried out triplicate for each sample.

The syringyl/guaiacyl ratio (S/G) was calculated by dividing the sum of peak areas from syringyl derivatives (S1-S15) by the sum of peak areas from guaiacyl derivatives (G1-G16). The cinnamic acid/guaiacyl ratio (C/G) was calculated by dividing the sum of peak areas from cinnamyl derivatives (*p*-coumaric acid/P18 and ferulic acid/G18) by the

sum of peak areas from guaiacyl derivatives (G1-G16). The compound notations G, S, and P have been used in previous studies,[57,62-64] and are defined in the Table 3.1.

3.3. Results and discussion

3.3.1. Bonding properties

Figures 3.2 shows the weight loss during steam treatment and the shear strength of kenaf core composites in the different manufacturing conditions. It is obvious from Fig. 3.2 that the increase in steam-pressure with increasing pressing time causes an increase in the weight loss. The amount of weight loss was 1.0% for kenaf core composites at steam treatment of 1 MPa/1 min, whereas it increased to 16.0% at treatment of 1.5 MPa/7 min.

Hydrolysis of hemicelluloses produced the water-soluble components during steam or heat treatments. Some extractives and volatile degradation products were distilled in the steam during the process. Therefore, increase in steam-pressure and pressing time caused increase in the weight loss, indicating the degree of degradation of chemical components. Lawther *et al.*[66] reported the similar trends for wheat straw after steam treatment at 120 °C for 15-300 min.

The bonding strength of kenaf core composites is clearly affected by the manufacturing process conditions, as shown in Fig. 3.2. The result showed that each of the steam-pressure condition required different optimum pressing time to obtain the highest bonding properties. The maximum value of shear strength at steam pressure of 1 MPa seemed to be achieved with pressing time of 10 min. Whereas, at a steam pressure of 1.5 MPa, the optimum pressing time was only around 1 min. The proper control of steam pressure and pressing time are the important point to obtain the optimum conversion of chemical components, resulting in high bonding properties.

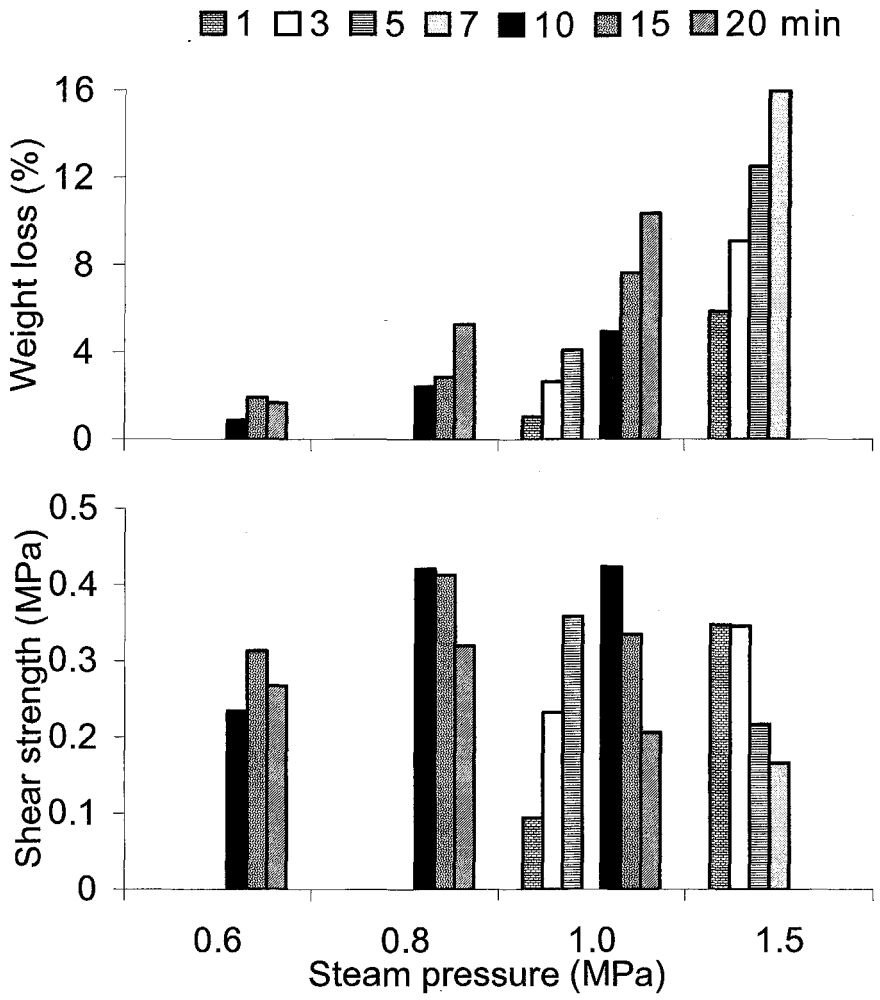

Fig.3.2 The effect of steaming condition on the weight loss and shear strength of kenaf core composites.

Figure 3.3 shows the relationships between shear strength and weight loss at the different steam-pressure and pressing time. The weight loss, that indicated degradation of chemical components, seemed to affect the bonding strength of kenaf core composites significantly. The optimum condition observed in this study was in the steam-pressure range of 0.8-1.0 MPa for 10-15 min, which provided around 0.40-0.42 MPa of shear strength and 2-5% of weight loss. At steam-pressure of 1 MPa for 1 min, the weight loss

was around 1% and the shear strength was only about 0.1 MPa. Whereas, after steaming for 20 min, the weight loss increased to around 16% and the shear strength decreased to about 0.2 MPa. It showed that if the amount of degradation products was too low, the composite products had poor bonding quality. On the other hand, severe conditions of steam treatment caused great degradation of chemical components, providing weak composite products. The color of the steam treated kenaf core composites was dark brown and became darker along with increase in steam pressure and pressing time, indicating a high degree of hydrolysis or modification of chemical components occurred during the treatment.

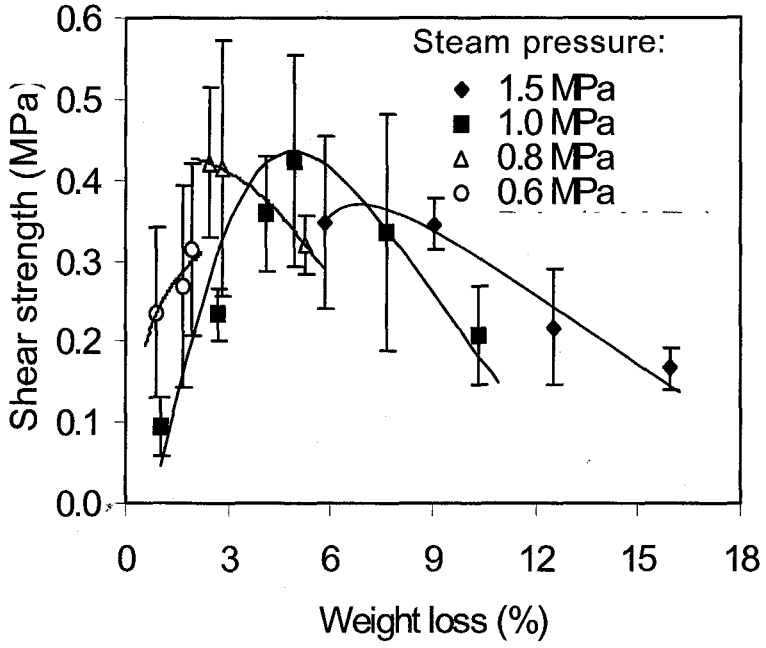

Fig 3.3 Relationships between shear strength and weight loss after steam treatment. Vertical lines through the data represent the standard

In chaper 1, it was found that mild steam treatment with the pressure range of 0.6 and 1 MPa caused to degrade not only hemicelluloses, but also lignin and cellulose of kenaf

core. During steam treatment, hemicelluloses hydrolyzed to produce water-soluble components and other decomposition products. Inoue et al.[18] found that at temperature between 180 °C (1 MPa) and 200 °C (1.5 MPa), the lignin-hemicelluloses matrix of solid wood became thermoplastic and will deform to a different matrix under heat and pressure. Lignin is deposited in the cell walls of kenaf core in association with hemicelluloses via different types of covalent linkages.[36] Therefore, it is necessary to include these linkages in any discusson on the degradation of hemicelluloses and lignin.

3.3.2. TMAH/Py-GC-MS analysis

To discuss the role of cinnamic acids during steam treatment, the presence of cinnamic acids in the untreated and steam-treated samples were analyzed by TMAH/Py-GC-MS.

Figure 3.4 and Table 3.1 shows that the TMAH products from kenaf core and steam-treated samples consist of methylated syringyl, guaiacyl and *p*-hydroxyphenyl derivatives. The presence of the cinnamyl derivatives (P18; *p*-coumaric acid and G18; ferulic acid) supports their identification in other non-woody plants.[62-64] Figure 3.4 shows that *p*-coumaric acid exists in greater amounts than ferulic acid, which is consistent with the previous results.[39,58]

The S/G values decreased with increase in pressing time and steam-pressure, as shown in Fig. 3.5. This could be a result of the higher reactivity of syringyl moieties relative to guaiacyl derivatives during steam treatment. The S/G ratio of untreated kenaf core in this experiment was 1.81. This value was slightly higher compared with other results using TMAH-Py-GC-MS, however, it agreed well with the S/G ratio obtained by CuO oxidation method for the same species.[58]

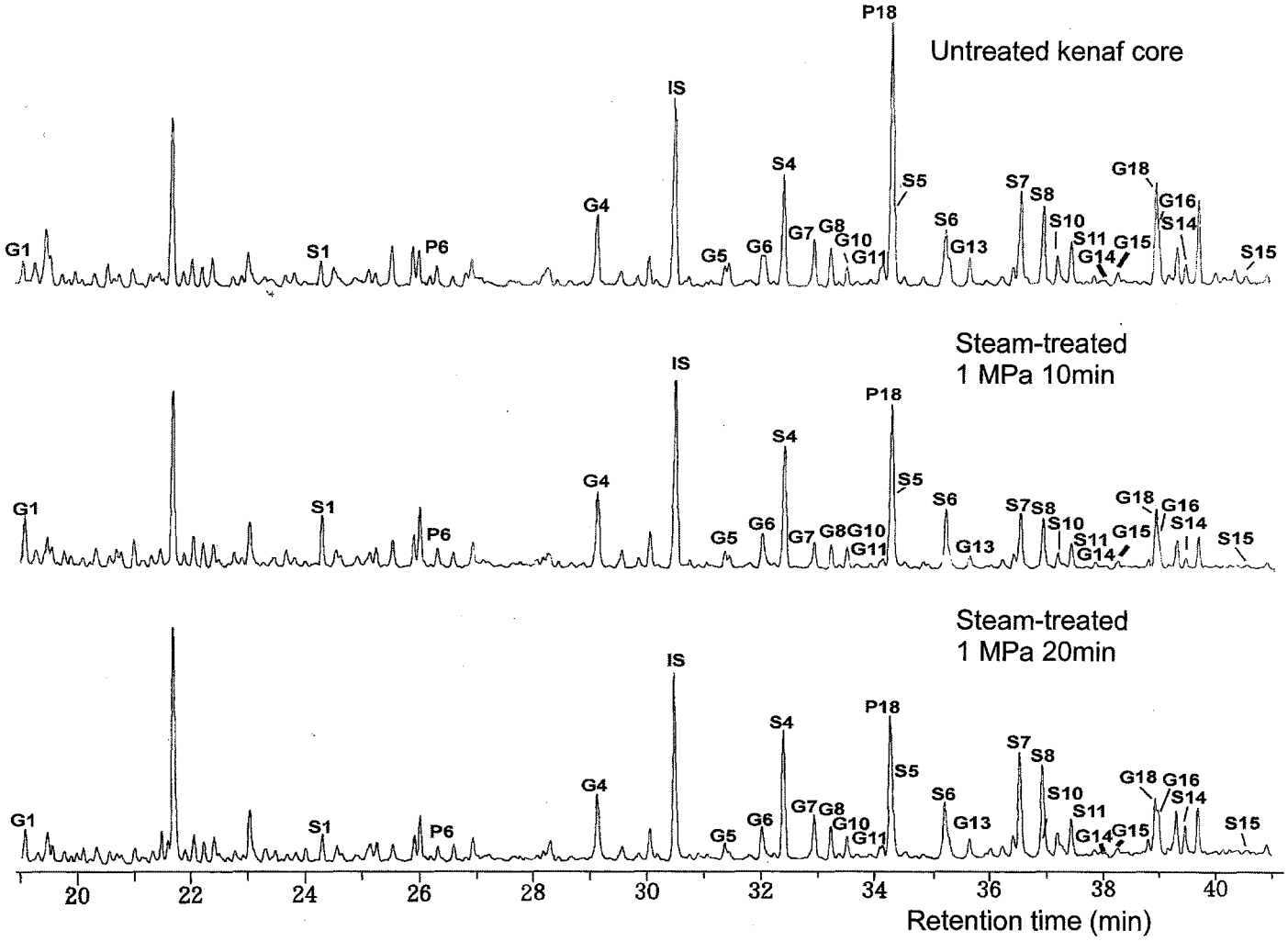

Fig 3.4 Chromatogram of the total ion current (TIC) for the TMAH Py-GC-MS products from untreated kenaf core and steam-treated kenaf core composites. Peak assignments are listed in the Table 3.1.

Table 3.1. List of products detected by TMAH Py-GC-MS

Notation	Assignment	Retention time, min	m/z (relative intensity)
G1	1,2-dimethoxybenzene	19.1	138 (M^+, 100), 123 (53), 95 (44), 77 (49), 65 (22), 52 (32), 51 (24), 50 (15), 41 (40)
S1	1,2,3-trimethoxybenzene	24.3	168 (M^+, 100), 153 (77), 125 (45), 110 (55), 95 (28), 93 (36), 77 (14), 65 (20), 51 (27)
P6	methyl 4-methoxybenzoate	26.4	166 (33), 136 (11), 135 (M^+, 100), 107 (16), 92 (14), 77 (28), 64 (12), 63 (10), 50 (10)
G4	3,4-dimethoxybenzaldehyde	29.1	166 (M^+, 100), 165 (66), 151 (14), 95 (29), 79 (16), 77 (30), 52 (16), 51 (33), 41 (23)
IS	3-ethoxy-4-methoxybenzaldehyde	30.5	180 (M^+, 46), 152 (47), 151 (100), 123 (10), 109 (12), 77 (9), 79 (8), 52 (11), 51 (19)
G5	3,4-dimethoxyacetophenone	31.4	180 (M^+, 45), 165 (100), 137 (20), 122 (11), 107 (7), 79 (17), 77 (18), 51 (18), 41 (45)
G6	methyl 3,4-dimethoxybenzoate	32.0	196 (M^+, 88), 165 (100), 137 (13), 125 (10), 122 (14), 94 (10), 79 (15), 59 (13), 51 (20)
S4	3,4,5-trimethoxybenzaldehyde	32.4	196 (M^+,100), 181 (51), 125 (39), 110 (29), 93 (19), 77 (11), 65 (14), 53 (15), 51 (17)
G7	cis-2-(3,4-dimethoxyphenyl)-1-methoxyethylene	32.9	194 (M^+,100), 179 (55), 151 (49), 148 (12), 121 (17), 107 (15), 91 (32), 77 (15), 51 (19)
G8	trans-2-(3,4-dimethoxyphenyl)-1-methoxyethylene	33.2	194 (M^+,100), 179 (59), 151 (45), 148 (15), 121 (13), 107 (14), 91 (38), 77 (18), 51 (21)
G10	cis-1-(3,4-dimethoxyphenyl)-1-methoxy-1-propene	33.5	208 (M^+,100), 194 (15), 193 (99), 165 (18), 133 (29), 105 (26), 91 (19), 79 (22), 77 (25)
G11	trans-1-(3,4-dimethoxyphenyl)-1-methoxy-1-propene	34.2	208 (M^+,100), 193 (68), 165 (37), 105 (21), 104 (15), 91 (14), 79 (19), 77 (21), 51 (14)
P18	4-methoxycinnamic acid, methyl ester	34.3	195 (26),192 (M^+, 71), 161 (100), 134 (19), 133 (46), 89(16), 77(14), 63 (14), 43 (23)
S5	3,4,5-trimethoxyacetophenone	34.4	210 (M^+,70), 195 (100), 139 (18), 137 (14), 124 (14), 109 (18), 66 (19), 53 (15), 43 (62)

S6	methyl 3,4,5-trimethoxybenzoate	35.2	226 (M^+,100), 211 (57), 195 (28), 155 (28), 151 (16),125 (14), 124 (15), 59 (20), 53 (17)
G13	trans-1-(3,4-dimethoxyphenyl)-3-methoxy-1-propene	35.7	208 (M^+, 94), 181 (29), 177 (100), 146 (46), 131 (29), 91 (22), 77 (23), 51 (23), 45 (31)
S7	cis-2-(3,4,5-trimethoxyphenyl)-1-methoxyethylene	36.5	224 (77), 209 (M^+,100), 210 (12), 181 (16), 151 (19), 149 (11), 121 (15), 95 (10), 51 (10)
S8	trans-2-(3,4,5-trimethoxyphenyl)-1-methoxyethylene	36.9	224 (82), 209 (M^+,100), 210 (13), 151 (18), 149 (12), 121 (17), 95 (12), 53 (10), 51 (11)
S10	cis-1-(3,4,5-trimethoxyphenyl)-1-methoxy-1-propene	37.2	238 (86), 224 (13), 223 (M^+,100), 195 (15), 192 (22), 165 (21), 119 (20), 109 (12), 77 (13)
S11	trans-1-(3,4,5-trimethoxyphenyl)-1-methoxy-1-propene	37.4	238 (89), 224 (16), 223 (M^+,100), 195 (17), 192 (25), 165 (15), 119 (18), 77 (11), 53 (13)
G14	threo/erythro-1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxypropane	38.0	270 (M^+,1),182 (13), 181 (100), 166 (14), 165 (13), 151 (16), 77 (14), 55 (16), 43 (37)
G15	threo/erythro-1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxypropane	38.3	270 (M^+,1),181 (100), 166 (11), 165 (18), 151 (9), 107 (2), 91 (3), 77 (4), 43(3)
G18	3,4-dimethoxycinnamic acid, methyl ester	38.9	222 (M^+, 100), 207 (19), 191 (60), 147 (21), 119 (17), 91 (14), 77 (15), 53 (17), 51 (31)
G16	cis-1-(3,4-dimethoxyphenyl)-1,3-dimethoxy-1-propene	39.0	238 (M^+,100), 223 (24), 207 (64), 191 (27), 176 (45), 103 (29), 77 (20), 75 (37), 45 (46)
S14	threo/erythro-1-(3,4,5-trimethoxyphenyl)-1,2,3-trimethoxypropane	39.4	300 (M^+,2), 212 (12), 211 (100), 196 (10), 181 (7), 167 (2), 125 (2), 53 (3), 45 (12)
S15	threo/erythro-1-(3,4,5-trimethoxyphenyl)-1,2,3-trimethoxypropane	40.5	300 (M^+,1), 212 (13), 211 (100), 196 (14), 181 (46), 167 (19), 77 (9), 55 (14), 45 (12)

G, guaiacyl units; S, syringyl units; P, *p*-hydroxyphenyl units; IS, internal standar

The cinnamic acids in the kenaf core were considered to be mostly ester-linked to some portion of the cell wall.[39] The C/G value of untreated kenaf core was 1.26, as shown in Fig. 3.5. It was found that the C/G values decreased with increase in pressing time and steam-pressure. This fact supported the hypothesis that some parts of ester-linked cinnamic acids were also susceptible to the cleavage by steam treatment, due to degradation of hemicelluloses and lignin. Binderless boards were usually made from non-wood lignocellulosic materials; therefore contribution of cinnamic acids in the self-bonding mechanism was also one of the important factors.

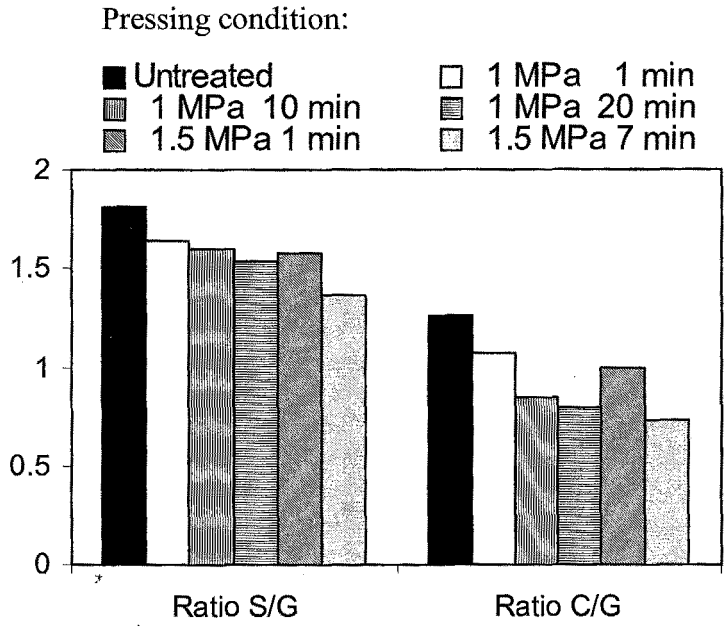

Fig. 3.5 Ratios of S/G and C/G of the kenaf core composites by TMAH/Py-GC-MS analysis. Results are given as relative percentage of total peak areas of TMAH/Py-GC-MS products from lignin. G, guaiacyl units; S, syringyl units; C, cinnamic acids units (*p*-coumaric acid + ferulic acid).

Figure 3.6 shows correlation between the ratio C/G and the bond strength of kenaf core composites manufactured at steam pressure of 1 MPa. It was shown that degradation of cinnamic acids would also contribute in the self-bonding of non-wood binderless composites. This phenomenon can be explained as follows; there are many possible chemical reactions taking place during steam treatment. In chapter 2, it was found that low-pressure steam treatment caused a significant effect on the degradation of three main components of kenaf core, providing good bonding performance. Considering that lignin was deposited in the cell walls of kenaf core in association with hemicelluloses via different types of covalent linkages[36], it was suggested that some parts of ester-linked cinnamic acids in the kenaf core were also cleaved during steam treatment. These reactions occurred simultaneously at varying degree of degradation during the treatment. Furthermore, it was believed that the degradation products would thermoset and crosslink into a new stable matrix under heat and pressure, acting as bonding and bulking agent to produce composite products.

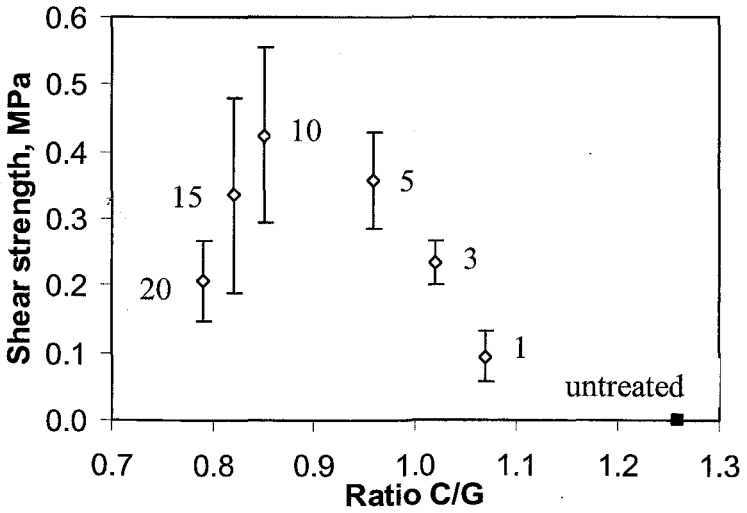

Fig 3.6 Relationships between ratio of cinnamic acids/guaiacyl (C/G) and shear strength. Vertical lines through the data represent the standard deviation. Number represent pressing time at 1.0 MPa (183 °C).

In order to analyze the bonding components, steam-treated samples from laminated kenaf core manufactured at steam pressure of 1 MPa for 10 min, were immersed in the hot water (70 °C) and cold water (20 °C) for 3 h. The result showed that the bonding properties of steam-treated samples after immersed in the cold water seemed to decrease significantly, although not delaminated. Otherwise, delamination occurs in the steam-treated sample after immersed in the hot water (70 °C) for 3 h. This fact realized that although the bond has good strength, it was still not resistant to water.

Figure 3.7 shows the chromatogram of the total ion current (TIC) for the TMAH/Py-GC-MS products for water-soluble fraction from laminated kenaf core after immersed in the hot water 70 °C and cold water 20 °C. It was clearly shown that the intensity of *p*-coumaric acid peak (P18) in the water-soluble fractions of 70 °C was higher than that obtained of 20 °C. Color of the hot water was darker than that of cold water, indicating the high degree of solubility of some bonding components in the hot water. It indicated that binderless kenaf core composites had relatively poor durability, as also found in previous study.[14]

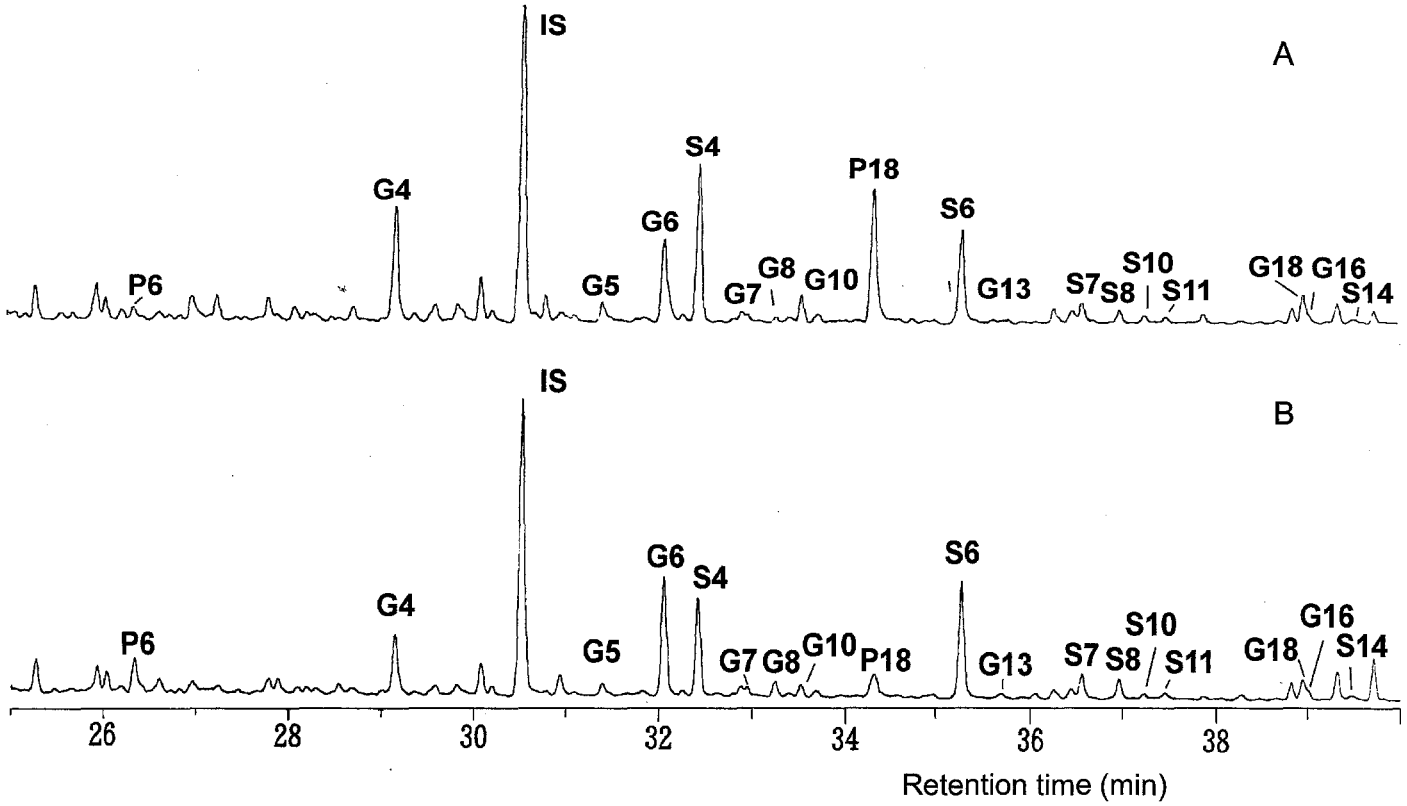

Fig 3.7 Chromatogram of the total ion current (TIC) for the TMAH Py-GC-MS products of water-soluble components from steam treated kenaf core composites after immersed in the hot water 70 °C for 3 h (A) and cold water 20 °C for 3 h (B). Peak assignments are listed in the Table 3.1.

Summary

In order to optimize degradation of chemical components of kenaf core, the proper control of high-pressure steam treatments became significant. In this study, the optimum bonding properties of kenaf core composites was obtained after steaming at 0.8-1.0 MPa for 10-15 min, which provided around 0.40-0.42 MPa of shear strength and 2-5% of weight loss.

Cinnamic acids, as postulated for cell wall of grasses/non-wood lignocellulosic materials, were identified by TMAH/Py-GC-MS analysis. The ratio of S/G and C/G decreased with an increase in pressing time and steam-pressure, indicating the modification and degradation of lignin has occurred. The result showed that some parts of ester-linked cinnamic acid were cleaved due to the degradation of hemicelluloses and lignin during treatment. Therefore, in addition to three main components, the cinnamic acid was also suggested to take place in the self-bonding mechanism of non-wood lignocellulosic binderless boards.

CHAPTER 4

PHYSICAL AND CHEMICAL PROPERTIES OF BAGASSE BINDERLESS BOARDS

4.1. Introduction

Sugarcane *(Saccharum officinarum L.)* stalk can be separated into the tough fibrous material called rind (approximately 50% of the total dry weight of stalk), the juice containing pith cells and internal fiber called pith, and the thin outer wax laden skin called dermax.[68] Bagasse, a waste of sugarcane processing, is one of the most promising non-wood lignocellulosic raw materials. Large quantities of this waste are still left unused or burnt in developing countries. The surplus bagasse is usually used as a fuel source for sugar processing. Many researches have been done to utilize the bagasse for production of ethanol, animal feeds, paper, and composite products.

Bagasse normally still contains residual sugars, depending on the cane variety, its maturity, harvesting method and the efficiency of the sugar milling plant. The residual sugars may cause problems in resin-bonded board manufacturing.[2] Sugars may not be chemically compatible with the conventional resin binders and may interfere the bonding.[2] The removal of pith/core and residual sugars is usually an important point to produce the good quality panel products.[2,68] Pith, which has no structural strength, is vey absorbent and can rob the boards much of applied resin.[69]

Considering that bagasse is one of the sugar containing lignocellulosic materials, Shen[2] developed the bagasse binderless composites using hot pressing system at an elevated temperature of 180 °C or higher. His research claimed that the bagasse binderless products could be produced without the removal of pith and residual sugars.

Mobarak *et al.*[3] has investigated the manufacturing of bagasse pith, bagasse depithed (rind) and whole bagasse molded binderless boards using hot pressing treatment under various pressing pressure of 15.7-25.5 MPa and temperature of 175-185 °C. The densities of these binderless molded products were relatively high, about 1.34 to 1.36 g/cm^3. Unfortunately, no data concerning the internal bond strength could be found in this study.

In chapter 2 and 3, the bonding characteristic of kenaf core binderless board has been investigated using chemical and spectroscopic analyses. Compared with wood, kenaf core was more easily degraded during steam-injection pressing, providing higher bonding performance.[60,70] In order to make clear the bonding characterization of non-wood lignocellulosic materials, bagasse binderless board will also be analyzed using the same procedures as kenaf core.

This chapter deals with manufacturing condition of the bagasse pith and bagasse rind binderless particleboards using steam-injection pressing, as well as the evaluation of hot-pressed particleboard as reference. First, the effects of the bagasse type, storage methods, and pressing condition on the mechanical of binderless boards are investigated. Afterthen, the chemical composition of bagasse and its binderless boards are analyzed and the self-bonding mechanism of non-wood materials is discussed.

4.2. Materials and methods

4.2.1. Raw materials

In order to investigate the effect of storage method, the raw materials were prepared as follows:

1. After harvesting, the sugarcane *(Saccharum officinarum L.)* stalk was directly separated by a cane separator to give inner (pith) and outer (rind) layers. The pith particles, was sent in the sugar milling process to extract the sugar juice. To eliminate

the effect of particle size, the bagasse rind was further processed into particles using hammer mill and then screened to pass 2 mm. The bagasse pith particles (C1) and rind particles (F1) were then air-dried.

2. After harvesting, the sugarcane stalk was separated by the cane separator. The pith particles was sent in the sugar milling process to extract the sugar juice, and then kept in the refrigerator (for ± 5 month), to prevent the effect of fermentation process. The pith particles obtained were then called C2.
3. The sugarcane stalk was stored for 3 weeks before prepared by the cane separator. Then after, the pith particles was sent in the sugar milling process to extract the sugar juice, and then air-dried (C3).

The moisture content of pith particles (C1, C2, and C3) and rind particles F1 were about 13%.

4.2.2. Manufacture of binderless boards

The dimensions of binderless boards were 230 x 230 x 12 mm. The bagasse rind F1 and pith C1 particles were hand-formed using a forming box into homogenenous single-layer mats. The mats were pressed using a steam-injection press, which was sealed with a 12-mm thick stainless steel frame. Steam was injected into the mats after the press had closed to the final board thickness and the pressing pressure reached the desired level set at 6.0 MPa. The mats were pressed with steam pressure of 1.0 MPa (183 °C) and pressing times of 0.75-15 min. After that, the steam was then released from the particle mats by using vacuum system for 3 min. During pressing, the temperatures of both the upper and lower platen were kept at 190 °C, which is a little higher than steam temperature, to avoid the steam condensation.

The target densities, material type, treatment type, and pressing times used in this experiment are shown in the Table 4.1. The target board densities of bagasse pith C1 and rind F1 were set at four levels, ranging from 0.5 to 0.8 g/cm^3. In addition, the binderless boards prepared by hot pressing were subjected to 190 °C for 10 min. In order to investigate the storage method, bagasse pith C2 and C3 binderless boards were manufactured under these conditions: steam-injection pressing (1.0 MPa for 10 min) and hot pressing system (190 °C for 10 min). The target board density was 0.7 g/cm^3.

4.2.3. Evaluation of physical properties of binderless board

Prior to evaluation of the mechanical properties and dimensional stability, the binderless boards were conditioned at room temperature for about 10 days. They reached a moisture content of 6 - 9%. The properties of binderless boards were evaluated in accordance with the Japanese Industrial Standard for Particleboards.[71]

Two specimens of 230 x 25 x 12 mm were prepared for each board for their static bending test. The three-point bending test was conducted over an effective span of 180mm at a loading speed of 10 mm/min. Three test specimens of 50 x 50 x 12 mm were prepared for each boards for internal bond (IB) tests, and two specimens of the same sizes from each boards were prepared for thickness swelling (TS) and water absorption (WA) tests after 24 h water immersion at 20 °C.

4.2.4. Chemical analysis of sugarcane bagasse

All samples were extracted successively with a mixture of ethanol and benzene (1:2, v/v) for 24h by refluxing, and then with distilled water at 85 °C for 3 h. The analyses of extractives were carried out in duplicates. Lignin and holocellulose contents were determined by Klason and Wise methods, respectively. α-cellulose content was

determined using the holocellulose by extraction with 17.5% NaOH. All the chemical analyses were carried out in triplicate.

The neutral sugar composition of the water-soluble fraction was determined as an alditol acetate by a gas chromatography (Shimadzu GC-17A, Shimadzu, Kyoto, Japan) on an ULBON HR-SS10 (0.25 mm x 25 m, Ulbon, Kyoto, Japan) after acid hydrolysis. The acid hydrolysis was carried out with trifluoroacetic acid (TFA) at 100 °C for 3h. The column oven temperature was programmed to increase from 30 °C to 210 °C at a rate of 4°C/min. All analyses were run in duplicate.

The bagasse (C1, C2, C3, and F1) particles and its binderless boards were then analyzed by TMAH/Py-GC-MS, as desribed in the section 3.2.4.

4.3. Result and discussions

4.3.1. Chemical properties of raw materials

The chemical composition of sugarcane bagasse based on the storage method and bagasse type is shown in the Fig. 4.1. The bagasse pith C1 particles and bagasse rind F1 showed no great differences in the chemical composition, except the hemicelluloses content of bagasse pith C1 were relatively high compared with that of bagasse rind F1. Compared with C1 and C2 particles, C3 particles contained the higher hot water-soluble components and the lower hemicelluloses. It seemed that the fermentation process had occurred during storage time. The color of bagasse pith C3 was pink, supporting this phenomenon. The fermentation process occurs in an exothermic process, thus rapidly increasing the temperature.[68] At the same time the residual free sugars ferments to acetic acid.[68] The combination cause in severe damage of hemicelluloses and cellulose fiber quality, as well as severe losses in storage.[68] Therefore, the fermentation process has to be controlled to preserve the quality of bagasse and to minimize losses in storage.

Table 4.1 Manufacturing condition for bagasse binderless particleboards

Raw materials	Target board density, g/cm^3	Treatment	Process condition	Pressing time, min					
Bagasse pith C1	0.5	SP	1 MPa			3	6	10	
	0.6		1 MPa	0.75	1.5	3	6^x	10^x	15^x
	0.7		1 MPa		1.5^{xx}	3	6^x	10^x	
	0.8		1 MPa			3^{xx}	6^{xx}		
	0.5	HP	190 °C					10	
	0.6		190 °C					10	
	0.7		190 °C					10	
	0.8		190 °C					10	
Bagasse rind F1	0.5	SP	1 MPa			3	6	10	
	0.6		1 MPa	0.75^x	1.5	3	6	10	
	0.7		1 MPa		1.5^x	3	6		
	0.8		1 MPa			3^x	6		
	0.5	HP	190 °C					10	
	0.6		190 °C					10	
	0.7		190 °C					10	
	0.8		190 °C					10	
Bagasse pith C2	0.7	SP	1 MPa					10	
	0.7	HP	190 °C					10	
Bagasse pith C3	0.7	SP	1 MPa					10	
	0.7	HP	190 °C					10	

SP= steam-injection pressing
HP= hot pressing treatment
^{x}The board was slightly delaminated
^{xx}The board was totally delaminated

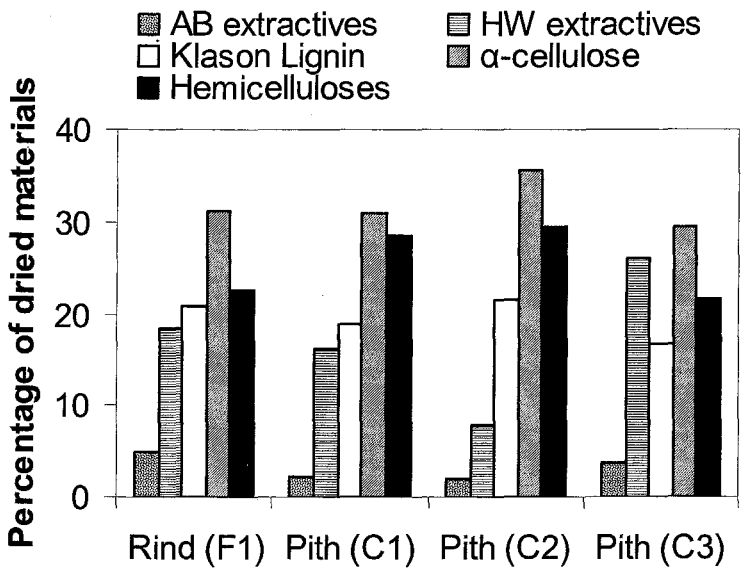

Fig. 4.1 Chemical composition of sugarcane bagasse

AB= alcohol benzene; HW= hot water

4.3.2. Properties of bagasse binderless board

Some of the steam-pressed binderless boards were slightly/totally delaminated after pressing, as shown in the Table 4.1. On the other hand, hot-pressed binderless boards were sound. One of the reasons may as follows: pith C1 binderless boards with higher densities have higher compaction ratios (i.e., 6.4 for a 0.60 g/cm^3 target density board), making it difficult for the steam inside the board to escape, providing poor bonding strength. It seemed that the delamination had already occurred during pressing treatment. In addition, C1 particles contained high water-soluble components, which indicated the high residual free sugars. The degradation of the chemical components and residual free sugars into low molecular weight compounds will release water during treatment.[2] Therefore, by injecting the high-pressure steam at longer pressing time, the excessive of steam would be produced and a great degradation of the chemical components would occur in the board. It was well

known that intensive degradation of chemical components during treatment might decrease the board properties.[19]

Steam-pressed rind F1 binderless boards with short pressing time (i.e., 0.75 min for a 0.60 g/cm^3 target density board) were delaminated, whereas steam-pressed boards with longer pressing time were not. It was obvious that a minimum pressing time was required to achive plasticization of the particle mats. There were differences between rind and pith binderless boards in the occurrence of delamination. It may due to the effects of the chemical and physical properties of the raw materials.

The properties of the slightly/totally delaminated specimens were excluded from the results of board properties.

4.3.2.1 Bending strength

The effects of board density, pressing condition, and materials type on the MOR of binderless boards during various pressing times are shown in Figure 4.2. The result shows that the bagasse pith C1 binderless boards have higher MOR values than the bagasse rind F1 boards on the both pressing methods. Mobarak *et al.*[3] found the similar trends, which bagasse pith molded products provided high bending strength compared with bagasse depithed products. In the pith area, the parenchyma cells are very large and thin-walled.[3] It seemed reasonable to suppose that the pith particles were more easily deformed and packed up closely than the rind particles, thus enlarging the self-bonding area.

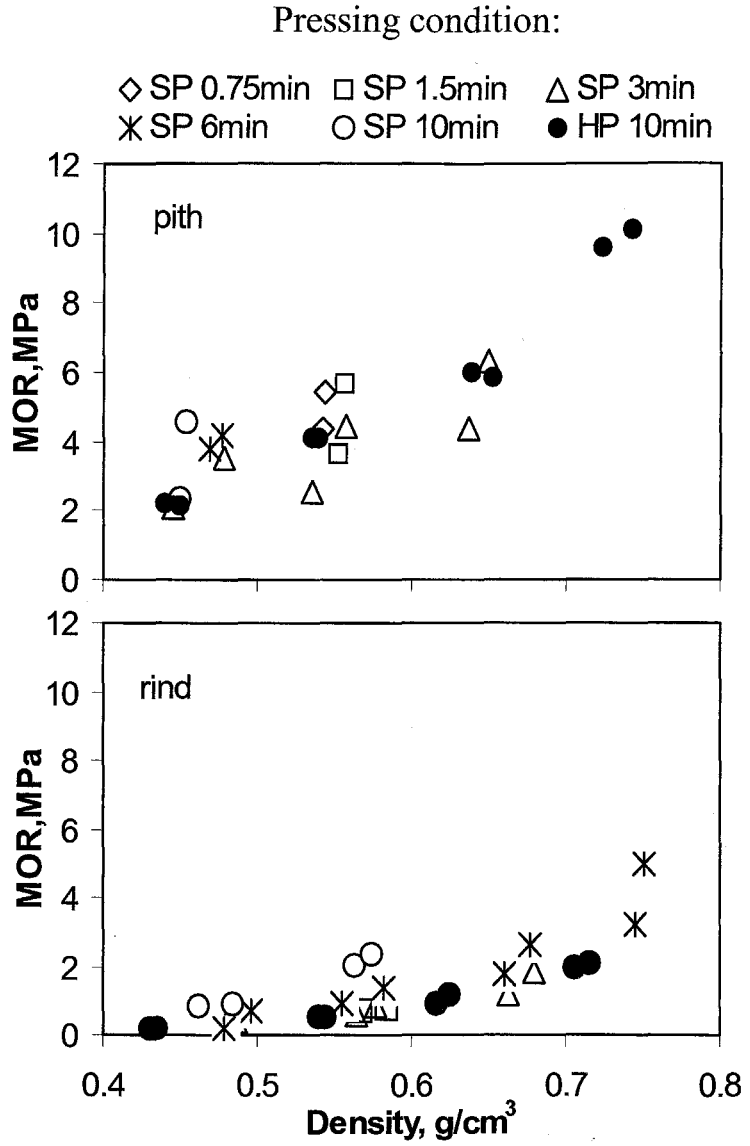

Fig. 4.2 Effects of board density, pressing condition on the MOR of bagasse pith C1 and rind F1 binderless particleboards. SP, steam pressure was 1.0 MPa; HP, hot pressing system at 190 °C

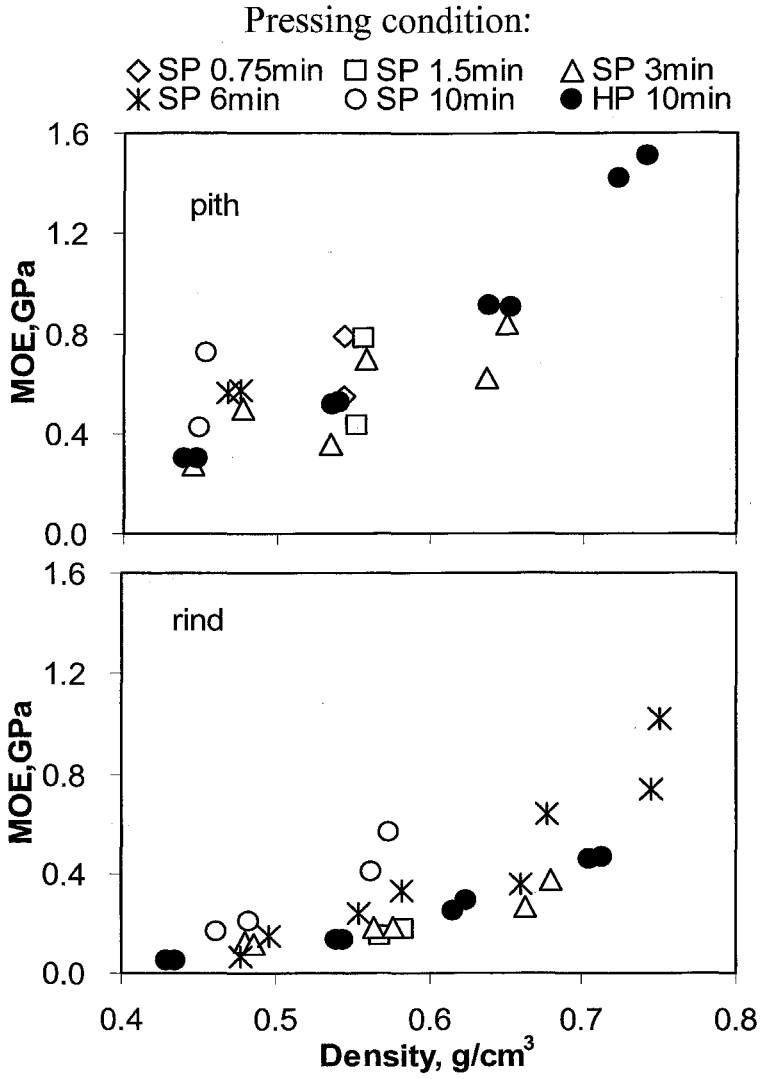

Fig.4.3 Effects of board density, pressing condition on the MOE of bagasse pith C1 and rind F1 binderless particleboards. SP, steam pressure was 1.0 MPa; HP, hot pressing system at 190 °C

The MOR value of the bagasse particleboards increased with increasing the board density, as a similar trend to that of the conventional particleboards. The MOR value was 2.2 MPa for hot-pressed board from C1 particles with a density of 0.45 g/cm^3, whereas it was 9.9 MPa for a board density of 0.75 g/cm^3. Compared with hot-pressed boards, the MOR values of steam-pressed boards that made at longer than 3-min pressing time, were relatively higher.

The effects of the board density, pressing condition, and type of materials on the MOE of binderless boards during various pressing times are shown in Figure 4.3. As the result of MOR, the pith C1 binderless boards provided higher MOE values than the rind F1 boards. Compared with hot-pressed boards, steam-pressed boards indicated the high value in relatively short pressing time.

Figure 4.4 shows the effects of pressing and storage methods on the MOR of bagasse pith binderless particleboards at a corrected density of 0.65 g/cm^3. The result showed that the MOR values of steam-pressed boards were higher than those of hot-pressed boards. The steam-pressed C1 board was delaminated, whereas the C2 board was not. It might due to the high content of hot water-soluble in the C1 particles, as discussed before. The boards from C3 particles provided the lowest MOR compared with the boards from C1 and C2 particles for the both pressing methods. It seemed that some degradation has already occurred during storage period, as mentioned before, therefore resulting poor bending strength of the particleboards.

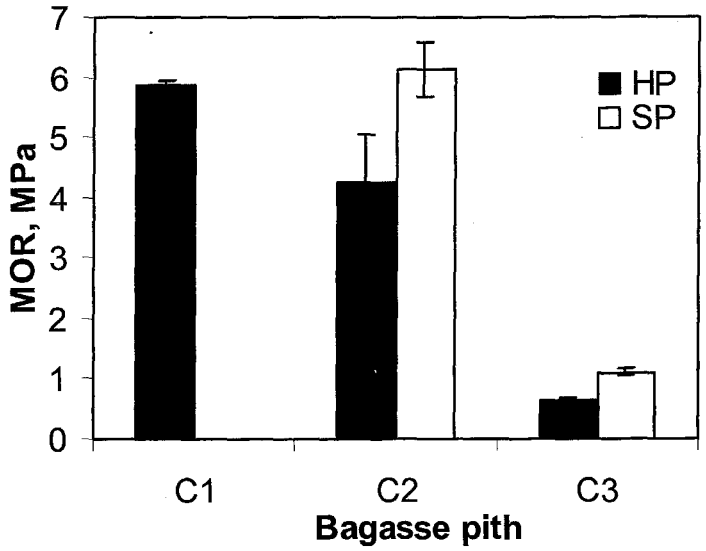

Fig. 4.4 Effects of materials type and pressing method on the MOR of bagasse pith binderless particleboards. The board density was a corrected value of 0.65 g/cm^3. *Vertical lines* through the bars represent the standard deviation from the mean. The pressing time was 10 min. SP, steam pressure was 1.0 MPa; HP, hot pressing system at 190 °C.

4.3.2.2 Internal bond strength

Effects of board density, pressing condition, and materials type on the IB strength of bagasse binderless boards are shown in Figure 4.5. Similar trends to MOR and MOE were observed for the IB. At a density of 0.45 g/cm^3, the IB value of hot-pressed board from C1 particles was 0.10 MPa, and at the density of 0.75 g/cm^3 it was 0.20 MPa. The IB values of steam-pressed boards that manufactured at longer than 3-min pressing time, were higher than hot-pressed boards. It showed that hot pressing system requires longer pressing time than steam-injection pressing to obtain the relatively same value of IB strength. The IB values of C1 binderless particleboards were lower than that of kenaf core binderless

boards,[14] at the same board densities, although it was still slightly higher than the other binderless boards, such as that from steam-exploded fibers of oil palm frond[9,19] and steam-injected wood MDF.[7]

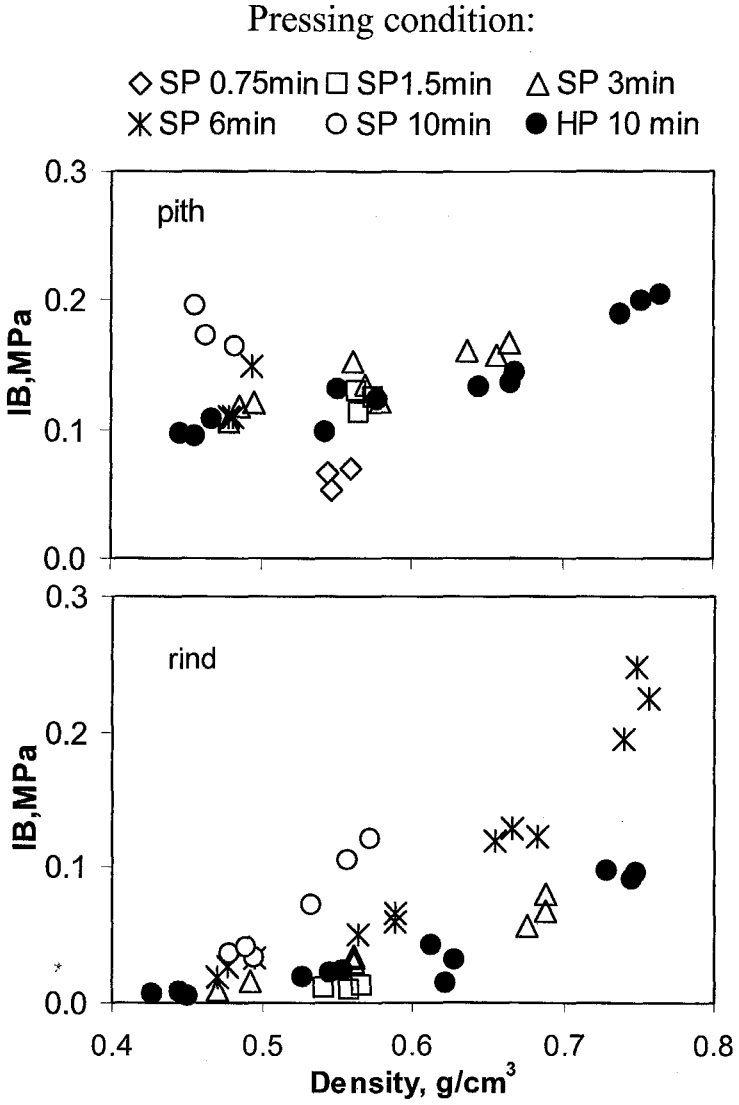

Fig.4.5 Effects of board density, pressing time and pressing method on the IB of bagasse pith C1 and rind F1 binderless particleboards. SP, steam pressure was 1.0 MPa; HP, hot pressing system at 190 °C.

The boards from C1 particles provided the higher IB values than the boards from F1 particles. It appeared that the pith particles were more easily deformed and packed up closely than the rind particles, as descibed previously. Another reason may be attributed to the higher hemicelluloses content of C1 particles than that of F1 particles. Degradation of hemicelluloses during treatment was believed to play an important role in self-bonding, as discussed in chapter 2. Ellis and Paszner[8] found that the board strengths were directly proportional to the pentosan content of the raw materials used.

Figure 4.6 shows the effect of pressing time on the IB of the binderless boards. The figure shows the corrected IB values for a board density of 0.55 g/cm^3. It is obvious that the IB values increase with increasing the pressing time. The delamination was observed in the binderless boards from bagasse pith pressed for more than 6 min. It seemed that the severe degradation of the chemical components had already occurred, as discussed previously. Suzuki *et al.*[19] reported that steam-exploded oil palm frond fiber at steam pressure of 3.0 MPa caused great damages in lignin macromolecules, and the binderless boards with poor quality were manufactured.

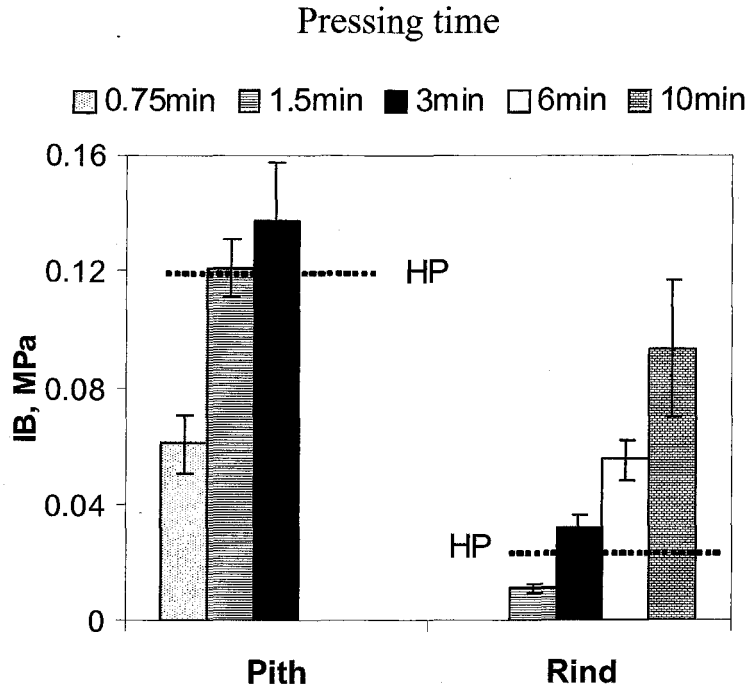

Fig.4.6 Effect of pressing time on the IB of bagasse pith C1 and rind F1 binderless particleboards. The board density was a corrected value of 0.55 g/cm^3. *Dotted lines* represent IB values of hot-pressed boards (HP) at 190 °C for 10 min. SP, steam pressure was 1.0 MPa.

Figure 4.7 shows the effects of pressing and storage methods on the IB of bagasse pith binderless particleboards at a corrected density of 0.65 g/cm^3. Similar trends to the MOR were observed for the IB. The values of steam-pressed boards were higher than those of hot-pressed boards. The bagasse pith C3 particleboards showed the lowest IB values compared with the other bagasse pith. Considering these results, the storage method is an important key to utilize bagasse as a raw material of binderless products.

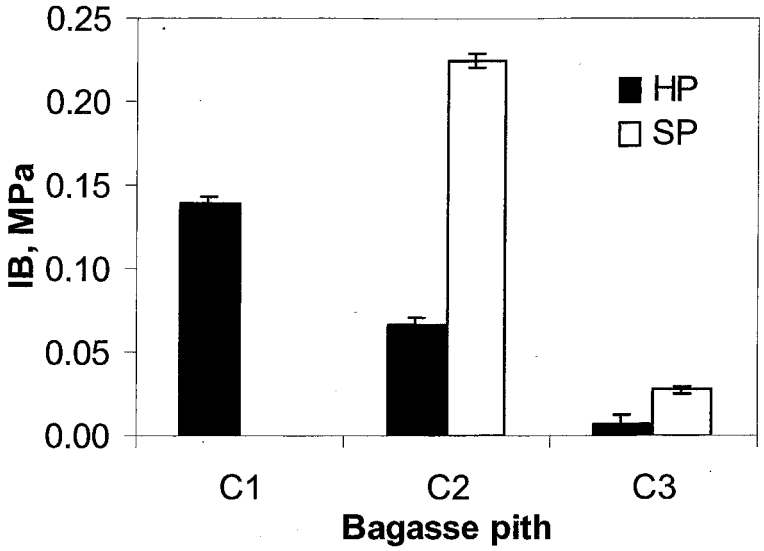

Fig. 4.7 Effects of materials type and pressing method on the IB of bagasse pith binderless particleboards. The board density was a corrected value of 0.65 g/cm^3. *Vertical lines* through the bars represent the standard deviation from the mean. The pressing time was 10 min. SP = steam pressure was 1.0 MPa; HP = hot pressing system at 190 °C.

4.3.2.3 Dimensional stability

The TS values of pith C1 and rind F1 binderless particleboards are shown in Figure 4.8. The results showed that no significant change was observed between the TS and board density, but the TS values are affected by the pressing time and pressing method. For steam-pressed C1 binderless boards, a TS value of 0.45 g/cm^3 density board for a 3-min pressing time was 125%, whereas the TS values decreased to 21% and 7% for a 6 and 10-min pressing time, respectively. The longer pressing time had a lower TS value, as reported in the previous studies.[3,13] Samples of steam-pressed F1 binderless boards

manufactured at less than 3-min pressing time were broken into pieces after 24h water immersion, and thus no TS values could be obtained.

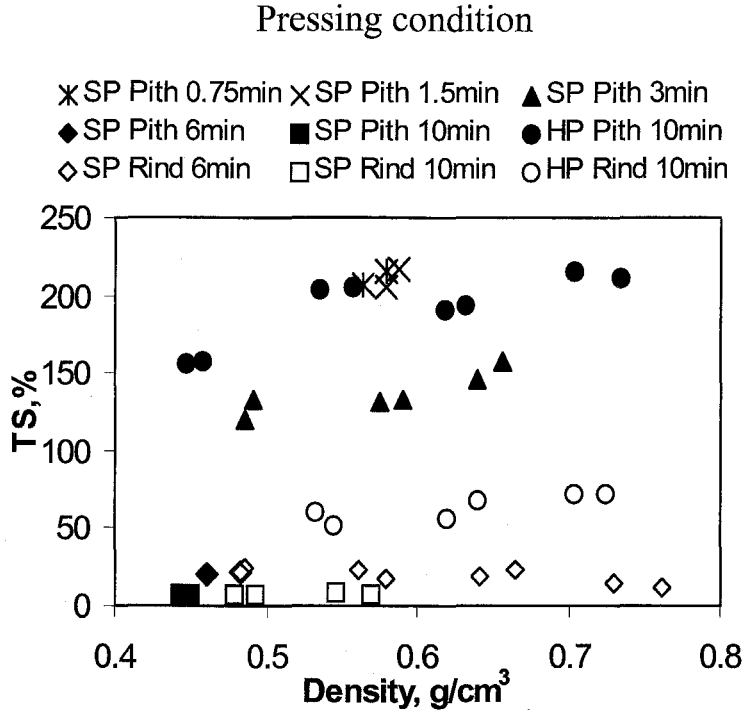

Fig.4.8 Effects of board density, pressing condition, and bagasse type on the TS values of binderless particleboards. Steam-injection was 1.0 MPa; HP = hot pressing system at 190 °C.

Compared with the hot-pressed boards, the TS values of the steam-pressed boards were much lower. The low TS value might be attributed to the steam-injection pressing method, which had proved to increase the dimensional stability of binderless boards.

The WA values of C1 and F1 binderless particleboards are shown in Figure 4.9. The WA decreased with increasing board density because of the decrease of spaces in the boards with the increase of the density.

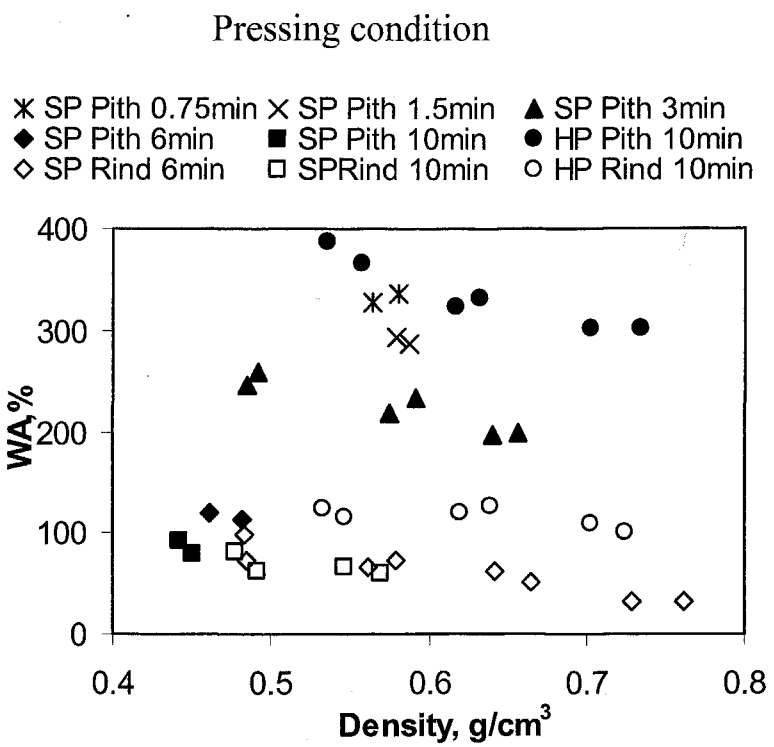

Fig.4.9 Effects of board density, steam pressing time and hot pressing system on the WA values of bagasse pith C1 and rind F1 binderless particleboards. Steam-injection was 1.0 MPa; HP = hot pressing system at 190^{0}C.

4.3.3 Chemical changes during steam/heat treatments

4.3.3.1 Chemical composition of binderless boards

Effect of hot pressing treatment on chemical composition of the bagasse pith C1 and rind F1 binderless boards is shown in Figure 4.10. The result showed that hot-pressing treatment caused no significant effects on the amounts α-cellulose and lignin of bagasse pith C1 and rind F1 binderless boards. However, the significant degradation of hemicelluloses in pith C1 board was found.

The amount of alcohol-benzene extractives of rind F1 particles was higher than that of pith C1 particles, indicating some waxes were still remained in the rind F1 particles.

Bagasse pith C1 and rind F1 contained relatively high water extractives. It seemed that residual free sugar was still high, as desribed by Shen.[2] The residual sugars in bagasse lead to foaming. Wet depithing of bagasse tends to produce less foam. In resin-bonded boards, residual sugars were not chemically compatible with the synthetic binders and interfere the bonding.[2] However, in binderless board, Shen suggested that during the hot moulding treatment, residual sugars, sugar polymers, furfural products and other decomposition products will transform, crosslink, and then thermoset.[2] The degradation of the chemical components and residual free sugars into low molecular weight compounds would release water during treatment. In this study, it was found that a special attention in the steam-injection pressing must be given due to the delamination of binderless boards could be occurred during high steam-pressure and longer pressing time, as desribed in the section 4.3.2.[73]

Figure 4.11 shows effects of pressing and storage methods on chemical composition of the bagasse binderless boards. The hemicelluloses and cellulose of bagasse pith C3 particles has degraded during storage period, as discussed previously. Therefore, the severe degradation of pith C3 components was found during steam and heat treatments.

The results also showed that there were similar trends for bagasse pith C1 and pith C2 particles after steam/heat treatments. Effect of steam-injection pressing was higher than hot pressing treatment on the chemical composition of bagasse binderless boards, as found in the kenaf core binderless boards. The surface of the steam-pressed boards was much darker than that of hot-pressed boards, indicating intensive changes in the chemical compositions of the lignocellulosic materials. Similar result was also found on the kenaf core, as described in the chapter 2.

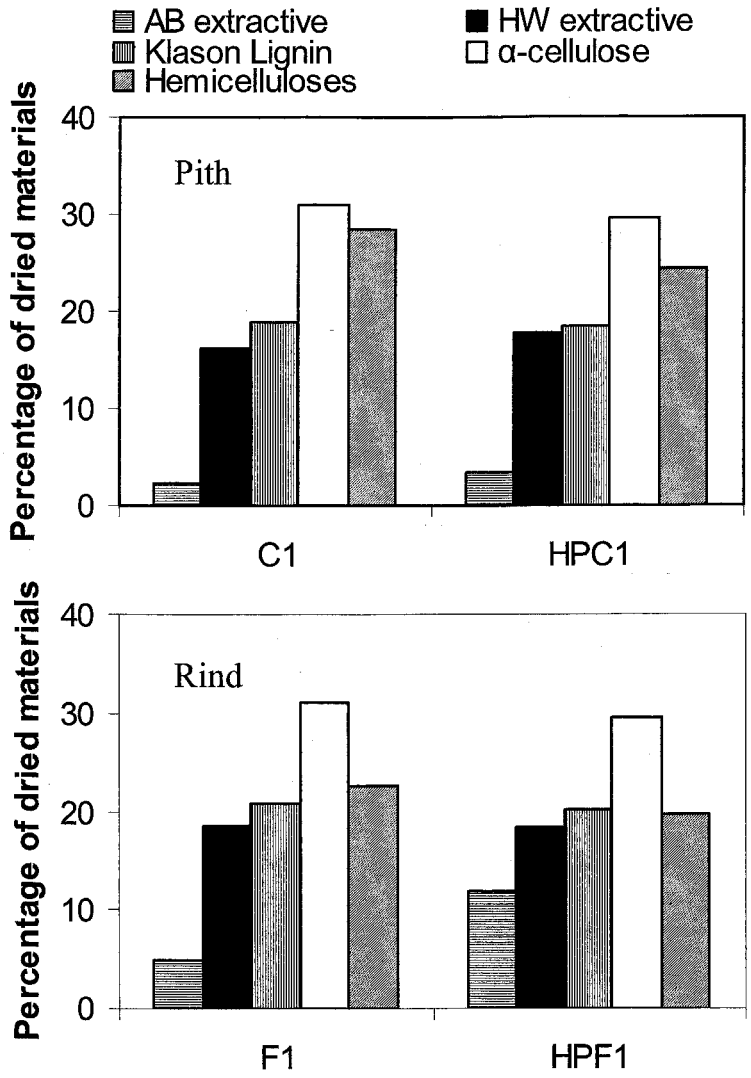

Fig. 4.10 Effect of hot-pressing treatment on chemical composition of binderless boards. Pressing time was 10 min, corrected board density was 0.65 g/cm^3. AB, alcohol-benzene; HW, hot water; HPC1, hot-pressed C1 board; HPF1, hot-pressed F1 board

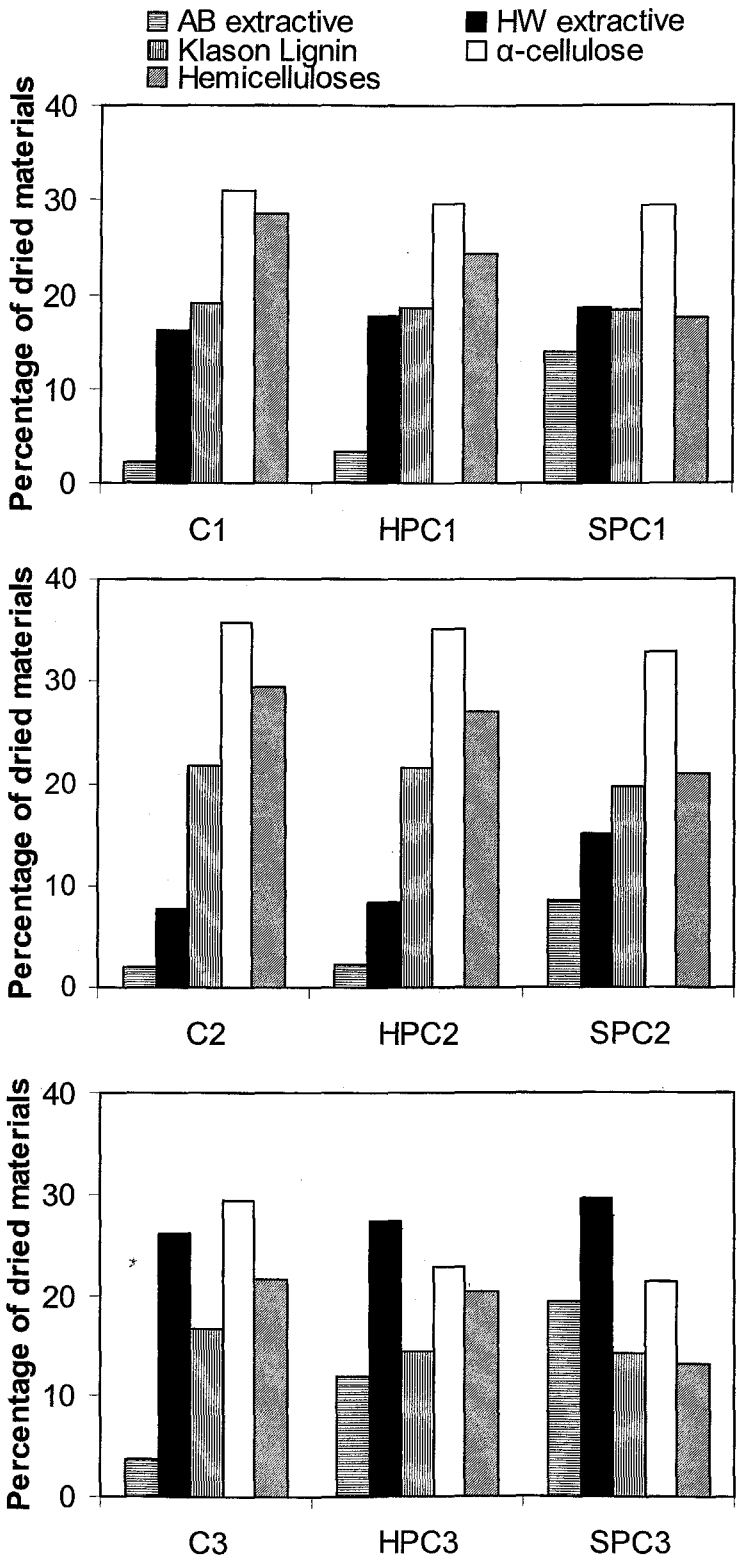

Fig. 4.11 Effects of pressing and storage methods on chemical composition of bagasse pith binderless boards. Pressing time was 10 min. AB, alcohol-benzene; HW, hot water; HP, hot-pressed boards; SP, steam-pressed boards

Figure 4.11 shows that hemicelluloses of bagasse pith C1 and C2 were more significant degraded than α-cellulose and lignin. Okamoto *et al.*[7] used steam pressing in a pressure range of 0.6 – 1.1 MPa for 5 min to produce dimensional stable binderless MDF. Under these conditions, hemicelluloses and cellulose decreased with increasing steam treatment, while the lignin component did not change significantly. In chapter 2 showed that hemicelluloses, α-cellulose and lignin of kenaf core decreased with increasing steam pressure and pressing time.

4.3.3.2 Analysis of water-soluble polysaccharide

The neutral sugar composition of water-soluble polysaccharide from bagasse and their binderless boards is shown in Table 4.2. The hemicelluloses in bagasse are composed of a xylan polymer backbone onto which other groups are bonded-mainly glucuronic acid and arabinose.[74] The hemicelluloses are associated with the cell wall, mostly soluble in alkali and easy hydrolyzed by an acid to simple sugars/sugar acids.[75]

The amount of xylose in the hot water extract of the bagasse pith C1 boards after steam treatment at 1 MPa was 6.67%, based on the dry weight of the original bagasse boards, while that obtained after hot pressing at 190 °C was 0.05%. Thus, marked differences were found in the amount of soluble xylan between the steam-injecting and hot pressing treatments. Similar trend also could be found in the amount of soluble xylan of the other particles.

High content of glucose in the water-soluble polysaccharide from untreated bagasse could indicate the residual free sugars content. Bagasse rind F1 particles showed higher glucose content than pith C1. It might due to the bagasse rind were not extracted for its sugar juice. Water-soluble polysaccharide from bagasse pith C3 contained high glucose

content. It might also come from degradation of cellulose, considering that bagasse pith C3 has degraded during storage period, as mentioned before.

Table 4.2 Neutral sugar composition of water-soluble polysaccharide*

	Rhamnose	Arabinose	Xylose	Mannose	Galactose	Glucose
C1	**	0.26	**	0.20	**	3.15
HPC1	**	0.45	0.05	0.28	**	4.88
SPC1	**	0.57	6.67	0.63	0.47	4.47
C2	**	0.25	0.04	0.30	0.09	1.89
HPC2	**	0.50	0.21	0.12	**	2.14
SPC2	**	0.75	6.08	0.56	0.50	2.62
C3	**	0.07	0.03	0.04	0.03	8.10
HPC3	**	0.29	0.15	0.31	**	8.64
SPC3	**	1.00	10.06	0.52	0.65	8.04
F1	**	**	**	**	**	6.46
HPF1	**	0.23	0.98	0.53	0.17	7.04

SP: steam-pressed boards manufactured at steam pressure of 1 MPa for10 min
HP: hot-pressed boards manufactured at temperature of 190 °C for 10 min
C1,C2,C3: bagasse pith
F1: bagasse rind
* percentage of dry-weight materials
** not detected

Hsu *et al.*[52] reported that xylose content in water extract from aspen treated by steam at 1.55 MPa for 4 min was 0.35%. Whereas, the amount of xylose in the water extract of kenaf boards after steam-injection treatment at 1 MPa for 20 min was 3.0%. Compared with those results, the hemicelluloses of bagasse seemed more easily susceptible to hydrolysis by steam. Kaar *et al.*[76] showed that processing optimums of steam explotion were highly raw materials dependent, since different carbohydrates composition dictated

different condition. Materials with high in xylose content required milder conditions, with shorter times, than materials with lower in xylose/higher in glucose.[76]

4.3.3.3 TMAH Pyrolysis GC-MS analysis

It was known that the structural features of lignin, such as the ratio of syringyl nuclei to guaiacyl nuclei and the amount of ring-conjugated carbonyl groups, had a great influence on the rate of the delignification reaction and the quality of the final products in the pulping process.[49] The combination of pyrolysis with high-resolution capilarry gas chromatography and mass spectrometry has been increasingly used for the determination of the chemical compositions of lignin in wood chemistry.[52] The analysis required only small sample size and a simple sample preparation. In this section, tetramethylammonium hydroxide (TMAH) was used as methylation agent to avoid the decarboxylation of polar moieties and yields phenolic derivatives, as desribed in the chapter 3.

The TMAH products from bagasse and its binderless boards consisted of methylated syringyl, guaiacyl and p-hydroxyphenyl derivatives. Figure 4.12 shows the chromatogram of the total ion current (TIC) for the TMAH/Py-GC-MS products for bagasse pith (C1) and rind (F1) particles. The syringyl/guaiacyl (S/G) ratios of bagasse and its binderless boards are shown in Table 4.4. The S/G ratios of bagasse C1, C2, C3, and F1 particles were 1.73, 1.84, 1.60, and 1.42, respectively. Sun JX *et al.*[49] found inhomogeneities in chemical structure of sugarcane bagasse lignin analyzed by nitrobenzene oxidation method. The seven-lignin fractions, isolated successively with alkali and alkali peroxide, were used in the research. The first four-lignin fractions were rich in syringyl units and contained large amounts of noncondensed ether structures, whereas the last three-lignin fractions had a high degree on condensation and were rich in guaiacyl lignins.[49]

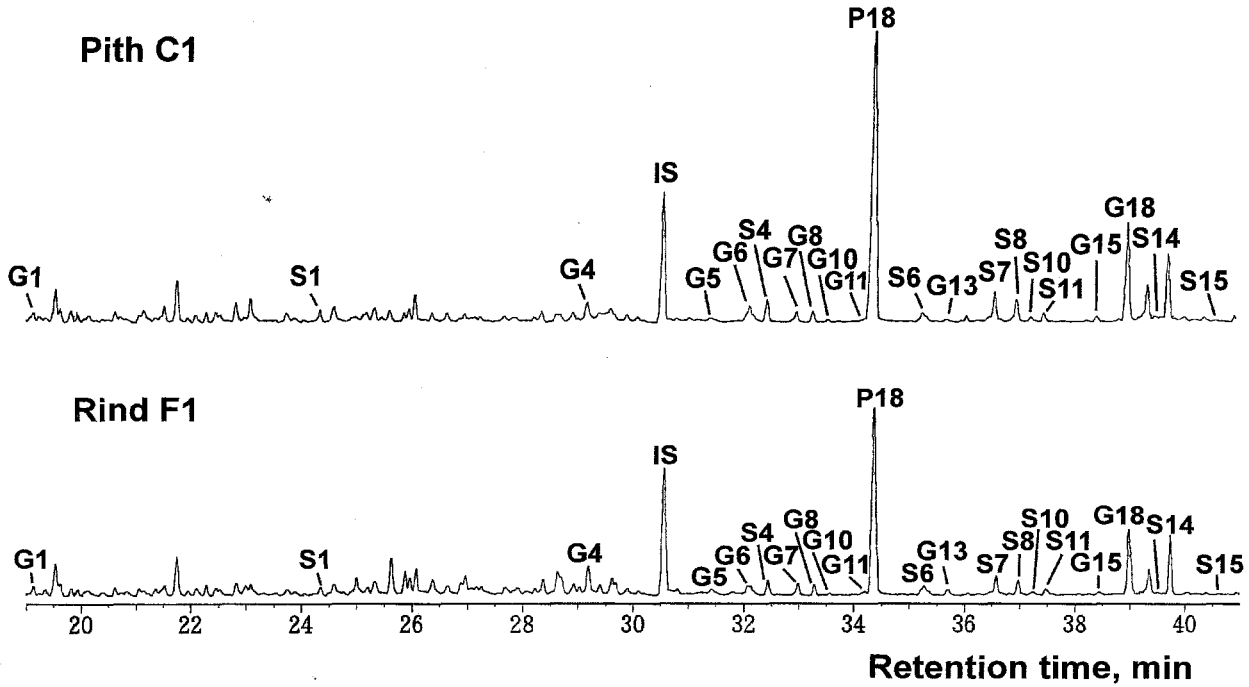

Fig. 4.12 Chromatogram of the total ion current (TIC) for the TMAH Py-GC-MS products from bagasse pith C1 and rind F1 particles. Peak assignments are listed in the Table 3.1.

Table 4.4 A S/G and C/G ratios of the bagasse and its boards by TMAH Py-GC-MS*

Sample	Ratio S/G	Ratio C/G
C1	1.73	9.97
HPC1	1.52	9.89
SPC1	0.86	6.59
C2	1.84	10.59
HPC2	1.49	10.20
SPC2	1.37	7.96
C3	1.60	9.46
HPC3	1.47	9.26
SPC3	1.37	8.47
F1	1.42	6.59
HPF1	1.06	5.44

G, guaiacyl units; S, syringyl units; C, cinnamic acids (*p*-coumaric acid + ferulic acid) units. C1,C2,C3: bagasse pith; F1: bagasse rind
SP: steam-pressed boards manufactured at steam pressure of 1 MPa for10 min;
HP: hot-pressed boards manufactured at temperature of 190 ^{o}C for 10 min
*as relative percentage of total-ion areas of TMAH/Py-GC-MS products

The S/G ratios were decreased during steam/heat treatments. It showed that syringyl units were more reactive than guaiacyl units, due to the more highly condensed structures of the G units than those of the S units. Steam-pressed boards had S/G ratios lower than hot-pressed boards. Compared with bagasse, a S/G ratio in the hot pressed kenaf boards was found to be close to that of original kenaf core, demonstrating that chemical modification of lignin by hot pressing is not as marked as that observed in the steam treatment.

The C/G values of untreated bagasse and its binderless boards are shown in Table 4.4. The presence of cinnamyl units (*p*-coumaric acid and ferulic acid) supports their

identification in non-woody plants.[58,63-65] The presence of *p*-coumaric acid exists in greater amounts than ferulic acid, which is consistent with other researchers.[49,77,78] Kato *et al.*[77] reported that the cinnamic acids in the sugarcane bagasse were considered to be esterified to the different moleculer species, polysaccharide and lignin nuclei, respectively. The result also showed that both linkages of lignin-carbohydrate and phenolic acid-carbohydrate were labile to alkali.[78]

The C/G ratios were decreased during steam/heat treatments, as shown in Table 4.4. Steam-pressed boards had C/G ratios lower than hot-pressed boards. It suggested that some ester-linked were also cleaved due to the degradation of hemicelluloses and lignin during steam/heat treatments, as discussed in the chapter 3. Quantitative analysis is required to make clear the cleavage of cinnamic acids.

4.3.4 Self-bonding mechanism of non-wood lignocellulosic materials

4.3.4.1 Comparison between kenaf core and bagasse

In order to compare between kenaf core and bagasse, effects of chemical changes by steam/heat treatments on internal bond strength of both binderless boards are plotted in Fig 4.12. Kenaf core binderless boards were manufactured at steam-pressure of 0.6-1.0 MPa for pressing time of 7-20 min, while three kind of bagasse pith (C1, C2, and C3) and rind F1 binderless boards were manufactured at steam pressure of 1 MPa for 10 min. Hot-pressed kenaf core boards was subjected to 190 °C for 20 min, whereas hot-pressed bagasse boards was for 10 min.

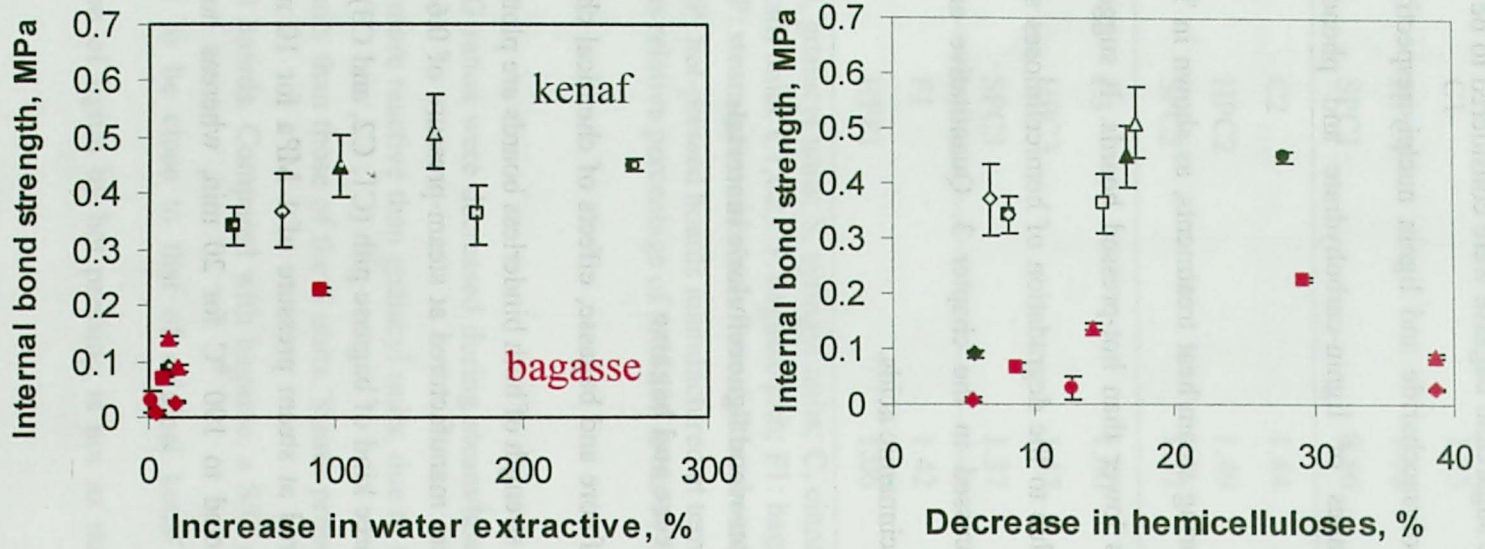

Fig. 4.12 Effects of chemical changes by steam/heat treatment on internal bond strength of binderless boards.

It was clearly found that degradation of chemical components of raw materials affected the self-bonding strength of binderless boards.[60,70] IB strength of bagasse binderless boards increased with the decrease of the amount of hemicelluloses and reached optimum when the amount of hemicelluloses decreased 30% than that of untreated bagasse. Severe degradation of hemicelluloses caused decreasing on IB strength of binderless boards. It should be noted that the IB strength of kenaf core boards was higher than that of bagasse binderless boards, although the same extent of chemical degradation was occurred. It might due to the hemicelluloses content of bagasse particles was lower than that of kenaf core particles, as shown in the Table 4.5. High content of glucose in the water-soluble component for bagasse indicate that the residual sugar is still high. It seemed that the residual sugar did not affect the bonding performance of binderless board.

Table 4.5 Chemical composition of kenaf core and bagasse pith

Chemical composition	Kenaf core	Bagasse pith
Water extractives, % DM	2.3	7.8
Neutral sugar, %DM		
Rhamnose	0.02	nd
Arabinose	0.01	0.25
Xylose	0.01	0.04
Mannose	0.04	0.30
Galactose	0.02	0.09
Glucose	0.09	1.89
Hemicelluloses, %DM	34.2	29.5
α-cellulose, %DM	36.1	35.7
Klason lignin, %DM	24.3	21.7
Ratio Syrigyl/Guaiacyl	1.81	1.84
Ratio Cinnamic acids/Guaiacyl	1.26	10.59

DM, dry-weight materials
nd, not detected

4.3.4.2 Self-bonding mechanism

In chapter 2, it was found that significant degradation of the chemical components of the kenaf core by the mild steam-injection treatments (0.6-1.0 MPa) increased the performance of the boards. This effect was not obtained by hot pressing treatments that degraded the chemical components of kenaf core much less effectively. Steam-injection pressing was an effective method to improve the bonding performance and dimensional stability of binderless boards. By injecting the high-pressure steam, the temperature of boards would rise immediately and the chemical components degraded in a short time range during treatment. Compared with kenaf core particleboards, bagasse particleboards had inferior properties. It showed that the chemical compositions of raw materials greatly affected the properties of binderless board, as well as manufacturing process, as discussed previously.

Based on those results, the self-bonding of non-wood lignocellulosic materials may be able to be explained as follows. During steam/heat treatments, chemical components would change in varying degree of degradation. Hemicelluloses hydrolyzed to produce low molecular weight polysaccharides and to increase their solubility in water, while cellulose was much more resistant to hydrolysis during steam. Analysis of water-soluble polysaccharides showed the increasing of xylose with increasing steam pressure and pressing time, indicating the hemicelluloses were degraded during steam and heat treatments. Decreasing amount of Klason lignin and S/G ratios indicated that modification and thermoplasticy of lignin was also occurred during steam/heat treatment. Ratios of C/G were decreased during steam/heat treatments, indicating some parts of ester-linked cinnamic acids were cleaved due to the degradation of hemicelluloses and lignin. All these degradation products are supposed to contribute in the self-bonding formation of binderless boards.

4.4. Summary

Binderless particleboards were prepared from bagasse pith and rind under various condition of steam-injection pressing. Effects of bagasse type, the pressing condition, and storage method on the mechanical and chemical properties of binderless boards were evaluated. Binderless boards manufactured by hot pressing method were also prepared. Based on the results obtained, the conclusions can be summarized as follows.

The bagasse pith particleboards provided higher properties than that of bagasse rind boards. The bagasse pith seemed more easily deformed than bagasse rind, thus enlarging the bonding area. The longer steam-injection time caused the delamination of the bagasse pith binderless boards, especially for high-density boards. It was suggested that the excessive of steam, which had been produced in the boards, would cause severe degradation of the chemical components, providing poor board properties. However, the steam-pressed boards showed relatively higher properties compared with hot-pressed boards. The storage method affected the chemical composition of raw materials and the board properties.

It was found that under steam-pressure of 1.0 MPa for 10 min, hemicelluloses of bagasse were more significant degraded than α-cellulose and lignin. Decreasing of S/G and C/G ratios indicated that modification of lignin had occurred during steam and heat treatments. Effect of steam-injection pressing was higher than hot pressing treatment on the chemical composition of bagasse binderless boards. Compared with kenaf core particleboards, bagasse particleboards had inferior properties. It may due to the hemicelluloses content of bagasse were lower than that of kenaf core. It also showed that the residual sugar in bagasse didn't improve the properties of binderless board. The extent of self-bonding formation depends on the chemical and morphological properties of lignocellulosic materials as well as on the manufacturing conditions.

CONCLUSIONS

This study aimed to investigate chemical changes of non-wood lignocellulosic materials during steam/heat treatment, in order to clarify the self-bonding characteristic of the binderless boards. For this objective, the chemical changes of kenaf core and bagasse binderless boards during steam and heat treatments were analyzed. Those binderless boards were manufactured using steam-injection pressing systems, as well as hot pressing system as reference. All these were discussed in the following chapters.

In chapter 1, the development of binderless boards and chemical changes during steam and heat treatments were discussed. It showed that the self-bonding mechanism was still unclear so far. Considering that binderless boards are usually made from non-woody materials, characterization of non-wood lignocellulosic materials was also discussed. Finally, the objectives of this study were clarified.

In chapter 2, effects of chemical changes in kenaf core binderless particleboards on the bonding performance and thickness swelling of boards were investigated by chemical and spectroscopic analyses. Boards were prepared by steam-injection pressing under the following conditions: 1 MPa for 7 - 20 min; 0.8 MPa and 0.6 MPa for 20 min. Boards prepared by hot pressing system were subjected to 190 °C for 20 min. The target density of all binderless boards was 0.55 g/cm^3. It was shown that mild steam-injection treatment (0.6-1.0 MPa) caused significant degradation of hemicelluloses, lignin and cellulose of kenaf core. Based on dry-weight of original material, the decrease of hemicelluloses (up to about 28%), α-cellulose (up to about 20%), lignin (up to about 18%) and increasing of water-soluble fractions (up to about 260%) by steam-injection pressing (0.6 – 1.0 MPa) can produce kenaf core binderless boards with relatively good quality.

Compared with steam-injection pressing, the conventional hot pressing caused a lower degree of degradation of chemical components. Neutral sugar composition of water-soluble polysacharide from hot-pressed boards was relatively similar with that of untreated kenaf core. In addition, lignin analysis by Pyrolysis Gas Chromatography Mass Spectrometry showed that syrigyl/guaiacyl (S/G) ratio of hot-pressed board was not different significantly with that of untreated kenaf core. The hot-pressed kenaf core binderless board showed poor bonding performance. Thus, it was found that partial degradation of the three major chemical components of the kenaf core by mild steam-injection treatment increased the bonding performance and dimensional stability of the binderless board, and gave better quality than those made by hot-pressing treatments.

Chemical analysis of kenaf core binderless particleboards showed that hemicelluloses, lignin and cellulose were significantly degraded during steam treatment. Considering that kenaf was one of the non-wood materials that contain hydrocinnamic acids, it was necessary to analyze the role of cinnamic acids during steam treatment. In addition, the proper control of high-pressure steam treatment is important to optimize the bonding performance of boards. Therefore, in the chapter 3, the optimum self-bonding condition of kenaf core composites by using steam treatment was investigated and the presence of cinnamic acids in the kenaf core and its composites was analyzed by pyrolysis gas chromatography-mass spectrophotometry in the presence of tetramethylammonium hydroxide (TMAH/Py-GC-MS). Two plies of laminated binderless kenaf core were treated by steam treatment under various conditions. The weight loss during steam treatment and the shear strength are then calculated.

The result showed that the optimum bonding properties of kenaf core composites were achieved under these conditions: steam pressure of 0.8-1.0 MPa and pressing time of 10-15 min were able to provided shear strength of 0.40-0.42 MPa while having 2-5% of

weight loss. The ratios of S/G and C/G decreased with increase in pressing time and steam-pressure, indicating the modification and degradation of lignin occurred. It concluded that some parts of ester-linked cinnamic acid were cleaved due to the degradation of hemicelluloses and lignin during treatment. The result also showed there were a correlation between decreasing of C/G ratio and shear streng of binderless kenaf core composites. Thus, in addition to three main components, the cinnamic acid was also suggested to take place in the self-bonding mechanism of non-wood lignocellulosic binderless boards.

In chapter 2 and 3, steam injection pressing system was proved to cause significant degradation of chemical components of the kenaf core, compared with hot pressing system. Based on those results, in chapter 4, the bonding characterization of bagasse binderless board would be analyzed using the same procedures. Bagasse, a waste of sugarcane processing, is one of the prospective non-wood materials. Until now, large quantitative of bagasse is still left unused. Binderless particleboards from sugarcane (*Saccharum officinarum L.*) bagasse were manufactured using steam-injection pressing, as well as hot-pressing method as reference. Bagasse was separated into inner layer (pith) and outer hard fibrous layer (rind). Effects of storage method, bagasse type and pressing method on the mechanical and chemical properties of binderless particleboards were investigated.

The result showed that the bagasse pith particles provided the better board properties than bagasse rind particles. It seemed that bagasse pith particles were more easily deformed than bagasse rind particles, thus enlarging the bonding contact area. Under steam pressure of 1 MPa for 10 min, hemicelluloses of bagasse were more significantly degraded than α-cellulose and lignin. Effect of steam-injection pressing systems was more marked than that of the hot pressing on the changes of chemical composition of boards. The result showed that storage method is one of the keys for using bagasse for production

composites. Compared with kenaf core particleboards, bagasse particleboards have inferior properties. It supposed due to the lower content of hemicelluloses in the bagasse compared with kenaf core. It also showed that the residual sugar in bagasse didn't affect for improving the properties of binderless board.

The self-bonding of binderless board was greatly affected by degradation of chemical components of materials during steam/heat treatment. Physical and chemical characteristics and structure of non-wood lignocellulosic materials are different from wood. The result of this study showed that chemical components of non-wood materials would change significantly in varying degree of degradation during steam/heat treatments. Not only hemicelluloses, other chemical components of non-wood materials were also degraded during steam/heat treatments. Some parts of ester-linked cinnamic acids, which have been postulated for cell wall of grasses/non wood materials, were cleaved due to the degradation of hemicelluloses and lignin. All these degradation products are supposed to contribute in the self-bonding formation of non-wood lignocellulosic materials.

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